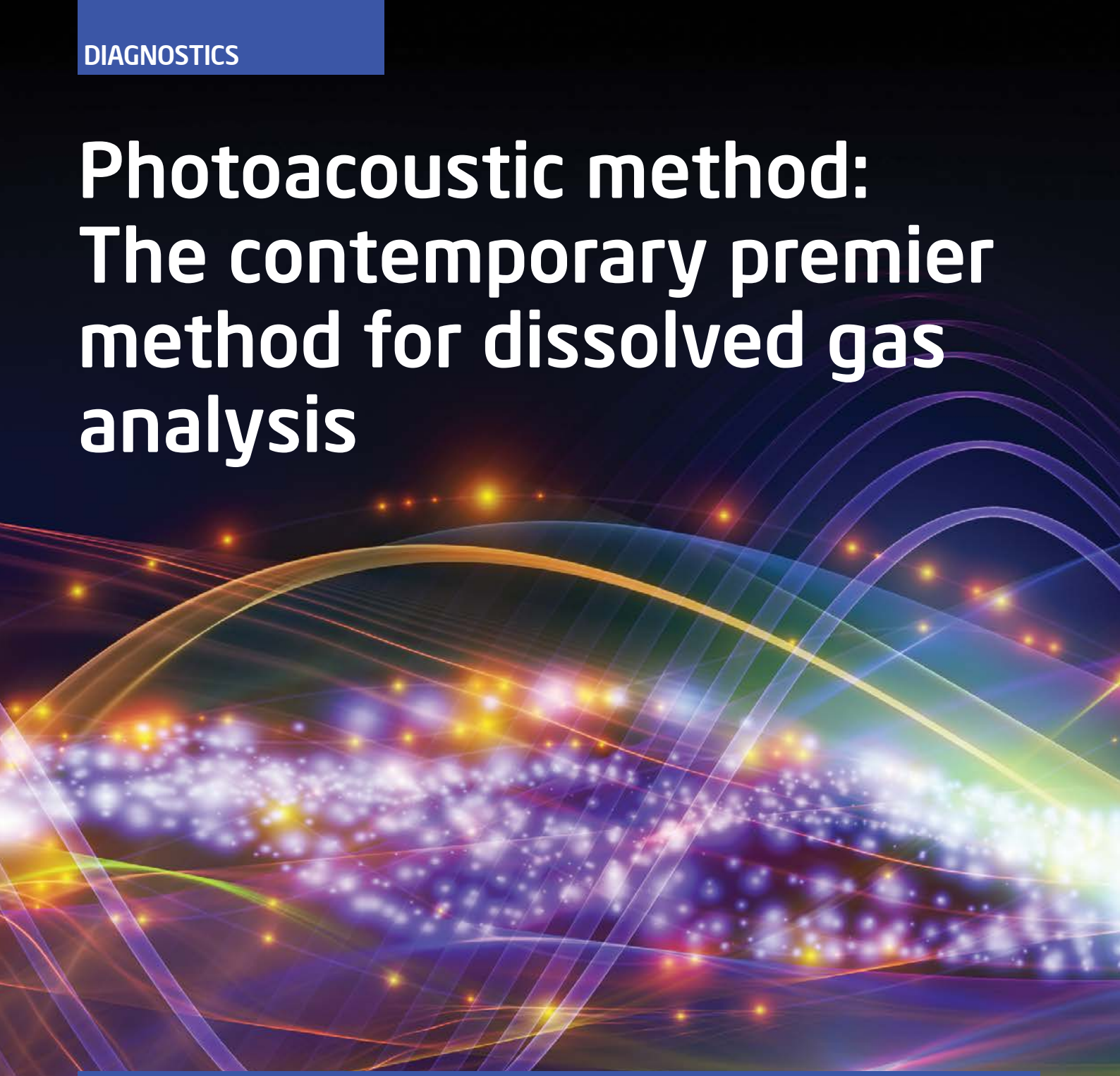
Photoacoustic method: The contemporary premier method for dissolved gas analysis



ABSTRACT

This article describes the tip of the iceberg of experience, research, debates, and understandings of photoacoustic spectroscopy applications since 2003 [13] when the first online and portable PAS devices appeared for dissolved gas-in-oil measurements.

After the introduction of the pros and cons of the general spectroscopic method for dissolved gas measurements in insulating liquids, in this column, we will dive into the method used probably in the majority of multi gas dissolved gas analyses in 2024 – the photoacoustic method (PAS). This column will describe the advantages and issues that users should be aware of when applying PAS for dissolved gas analysis (DGA). Along with PAS properties, it will include a short comparison with other DGA measurement approaches. It will also describe the main obstacles and challenges in becoming the ultimate gas detection and measurement for DGA measurement technique, as PAS has become in many other domains.

The study will briefly describe the main drives that bring PAS technology to the edge of measurements in different domains along with DGA applications. It will also review the new approaches for obtaining the main advantages of PAS application in dissolved gas analysis.

KEYWORDS:

Photoacoustic gas measurements, DGA, theory, history applications

Bell's invention of using light in the transmission of speech led to the method for detecting various gasses

From the first wireless phone to online dissolved gas analysis

After patenting the telephone in 1876, based on the invention of Antonio Meucci, Bell began focusing his attention on an ingenious concept—the use of light in the transmission of speech (Figure 1) [1]. The photosensitivity of selenium had been discovered in 1873, and in 1878, Bell began experiments to adapt this property to telephone transmission. Bell himself credited A. C. Brown of London for the first demonstration of the reproduction of articulate speech by the action of light upon selenium in a circuit with a battery and telephone. Yet the first well-documented evidence of speech transmission by means of light belongs to Bell and his assistant Charles Sumner Tainter, who were able to wirelessly transmit voice messages over around 213 m in June 1880.

Bell further discovered that the illumination of different solid substances th a rapidly interrupted beam of light energy resulted in the emission of acoustic energy at the same frequency as the modulation frequency.

Röntgen [2] and Tyndall [3] independently also shared the view that periodic heating and cooling of air in thermal contact with the disk caused sound production. They also showed that the phenomenon was not restricted to solid bodies and studied the effect of absorbing gases and vapours. Röntgen studied illuminating gas (coal gas) and ammonia, while Tyndall studied a large number of gases and vapours, including those from perfumes. Tyndall predicted that one variant of the method could be used to detect extremely small quantities of inflammable gases in mines [2].

The radiophonic (or photophonic) effect remained inactive for fifty years until it was revitalized by the work of Veingerov at the State Optical Institute in Leningrad

Revival as the optoacoustic effect and early 20th century applications

The radiophonic (or photophonic) effect remained inactive for fifty years until it was revitalized by the work of Veingerov at the State Optical Institute in Leningrad, where he focused on infrared gas analysis technology. Veingerov [4] explored the previous research by Röntgen and Tyndall on gases, noting Tyndall's forecast that the method could detect minute gas concentrations. In 1938, he published a paper in the Proceedings of the USSR Academy of Sciences (Russian: Doklady Akademii Nauk SSSR) entitled "A method of gas analysis based on the optico-acoustic Tyndall-Röntgen effect." This work, which utilized cutting-edge charged capacitive microphone diaphragms and a Nernst glower as a powerful blackbody infrared source, successfully measured CO_2 concentrations in N_2 as low as 0.2 vol. %. Through this, Veingerov significantly rekindled interest in the effect.

Gas detection may be achieved using a few main techniques. Although spectroscopic methods were developed concomitantly with chromatography ones, in the last half of the century, most industrial applications for this purpose were carried out by gas chromatography.

Photoacoustic spectroscopy (PAS) is an analytical technique that leverages the photoacoustic effect to analyze the properties of a substance. This technique

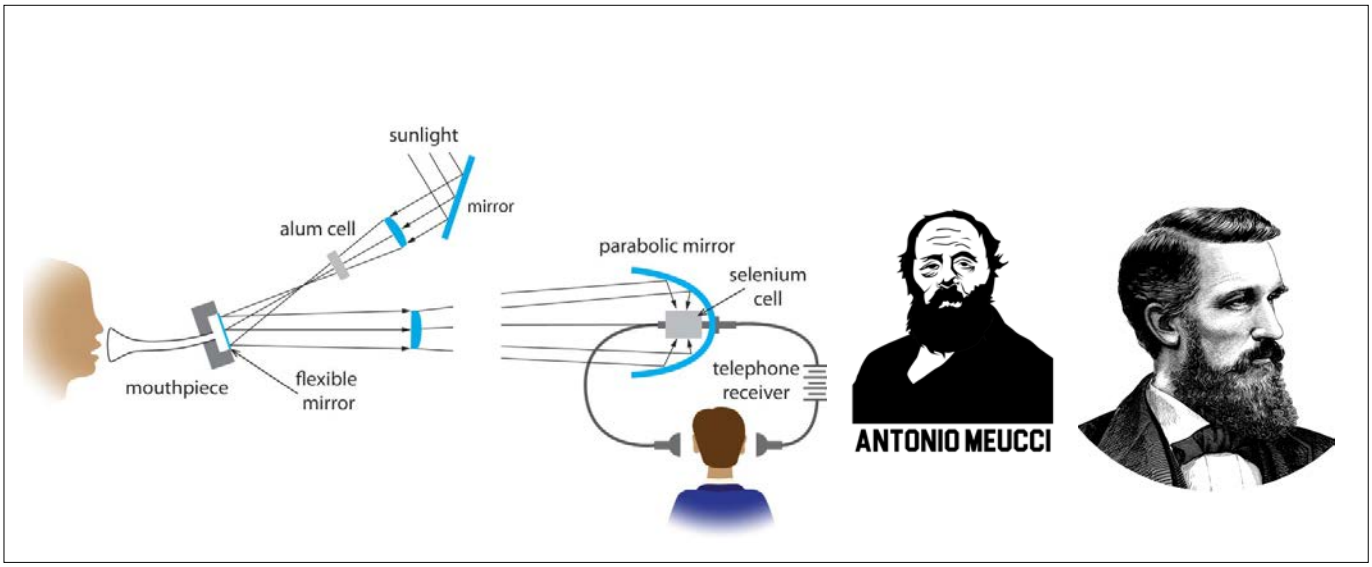


Figure 1. The photophone designed and built by Alexander G. Bell and Charles S. Tainer is considered the first implementation of wireless telephony or, in fact, of an optical communication device [12]

combines optical and acoustic methods to probe materials. When a sample is irradiated with modulated light (typically from a laser), it absorbs the light energy and undergoes nonradiative relaxation processes. This results in a localized temperature increase and subsequent thermal expansion, generating acoustic waves.

The acoustic waves are detected by sensitive microphones or piezoelectric transducers, and the amplitude of these waves is directly correlated to the energy absorbed by the sample. The spectral data obtained, referred to as the photoacoustic spectrum, plots the intensity of the acoustic signal against the wavelength of the incident light, providing qualitative and quantitative insights into the sample's composition.

Photothermal Techniques

Photoacoustic spectroscopy belongs to a broader category of photothermal techniques, where a light beam interacts with a sample, causing it to absorb the light and undergo changes in its thermal state. These changes may include variations in temperature, density, or other quantifiable properties of the material.

Detection can be achieved by experimentally measuring the temperature or density changes in the material, a method known as thermometric detection. Alternatively, if the light is modulated, causing the sample to alternately heat and cool rapidly, the sample may not have sufficient time to expand and contract physically. This rapid thermal cycling results in pressure fluctuations, which can generate sound waves. Such sound waves can be captured by sensitive microphones, piezoelectric devices, or through optical methods such as observing the deflection of a tightly focused beam of light reflected from the sample surface. These methods are more accurately described under the umbrella of photoacoustic techniques. Photoacoustic spectroscopy is often considered both a form of calorimetry and spectroscopy due to these characteristics.

Photoacoustic spectroscopy (PAS) is an analytical technique that leverages the photoacoustic effect to analyze the properties of a substance

Photoacoustic spectroscopy: Gases (Figure 3)

One advantage of photoacoustic spectroscopy is that it can be performed on all phases of matter. Figure 3 shows a general setup for the photoacoustic spectroscopy of a gas sample. A gaseous molecule that absorbs electromagnetic radiation is excited to a higher electronic, vibrational, or rotational quantum state. Generally, depopulation of this quantum state to lower-lying states occurs either via fluorescence or collisions, the latter giving rise to a temperature increase of the gas due to energy transfer to translation. This nonradiative relaxation process occurs when the relaxation time can compete with the radiative lifetime of the excited energy levels. Radiative decay has a characteristic lifetime of 10 -7 s at visible wavelengths as compared with 10-2 s at 10 μm. For nonradiative decay, these values depend on the pressure (decay time t inversely proportional to the pressure) and can vary strongly at atmospheric pressures (10-3–10-8 s). By modulating the radiation

By modulating the radiation source at an acoustic frequency, the temperature changes periodically, giving rise to pressure change, which can be observed as an acoustic signal

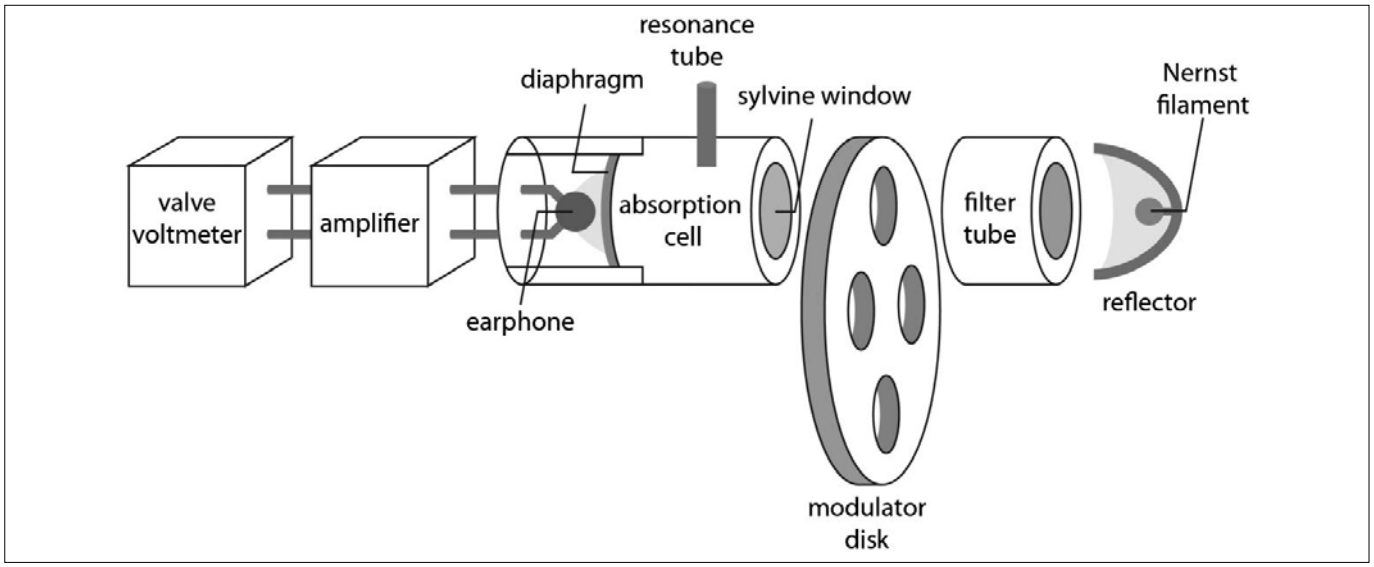


Figure 2. The optico-acoustic gas analysis apparatus developed in Leningrad, USSR, in 1938 by Veingerov was the first widespread application of the photophonic effect [4 &12]

With the development of sophisticated radiation sources and measurement capabilities, the spectroscopic method took over in most applications in gas chromatography

source at an acoustic frequency, the temperature changes periodically, giving rise to a periodical pressure change, which can be observed as an acoustic signal. In the gas phase, the effect can be detected with a sensitive microphone.

The application of PAS for DGA

With the development of sophisticated radiation sources and measurement capabilities of light, radiation, sound, heat and minuscule pressure changes, the spectroscopic method took over in most applications in gas chromatography. The same considerations were applied at the beginning of the 21st century for dissolved gas analysis with the appearance of photoacoustic spectroscopy (PAS) as an alternative to gas chromatography [7 and 13]. The first commercial PAS devices for online and portable DGA applications were issued by Kelman [13] based on technology developed in Denmark. The first PAS with the capability to be implemented for DGA appeared in 1999 [14].

In this column, the principle of PAS will be described, together with its pros and cons, as well as the methodology and technologies used to overcome its obstacles. The reader shall consider this method as an extension particularly suitable for an online DGA device, which should be equipped with adequate functionalities and implemented by following procedures to fulfil the expectations.

Of course, the data published in the promotional brochure needs to be examined and considered in non-ideal scenarios. For example, when we acquire a new car, we consider the published fuel consumption data as guidance, and we all know that in everyday driving, the real data may be different.

A diagram of a standard photoacoustic analyzer shows infrared (IR) energy emitted from the source, which is directed into a measurement cell that houses a gas sample. This IR energy is intermittently pulsed through the rotation of a chopper wheel and is further filtered to generate both qualitative and quantitative acoustic signals within a specific bandwidth.

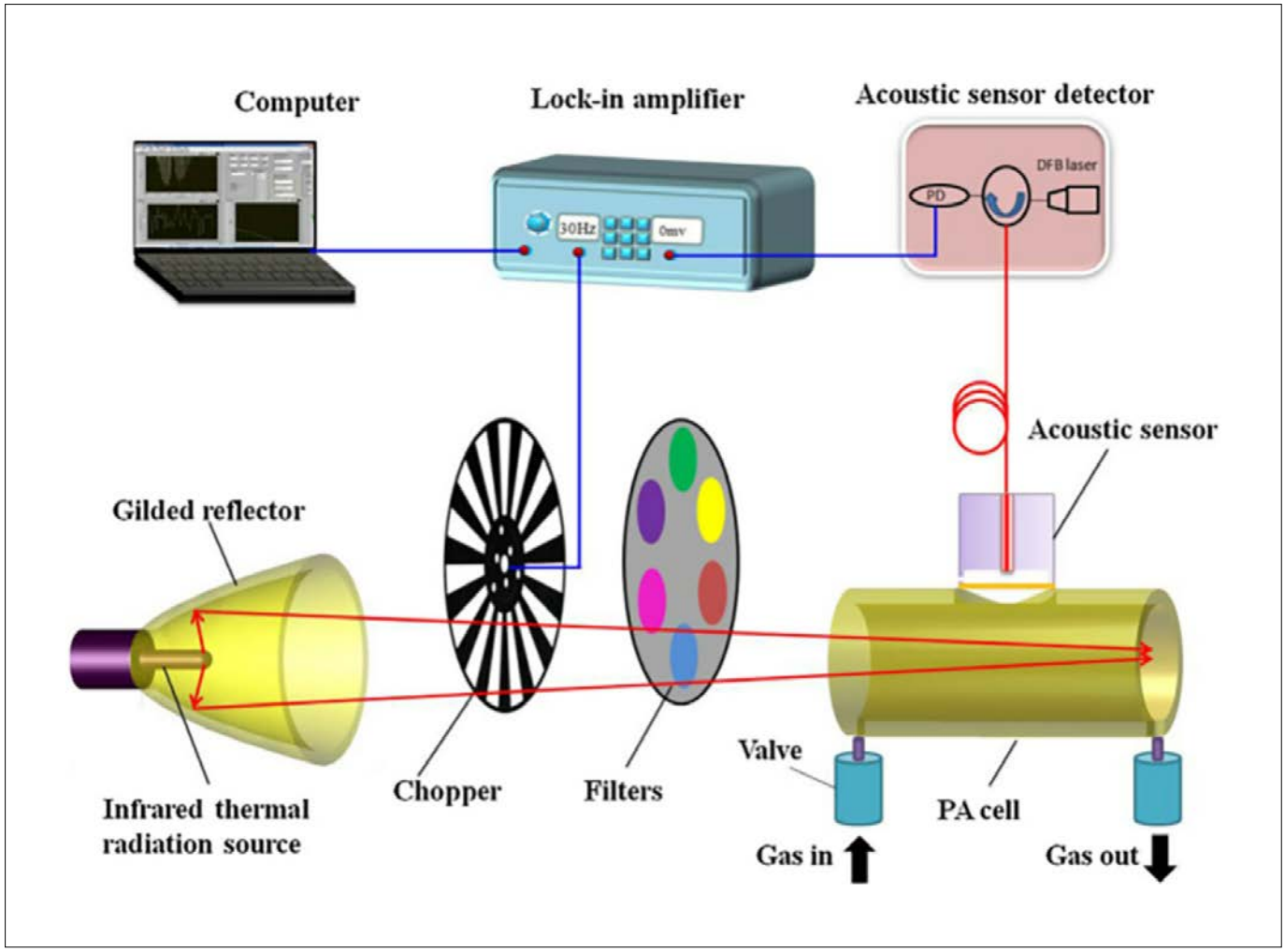


Figure 3. The schematic cell for gas measurement [6]

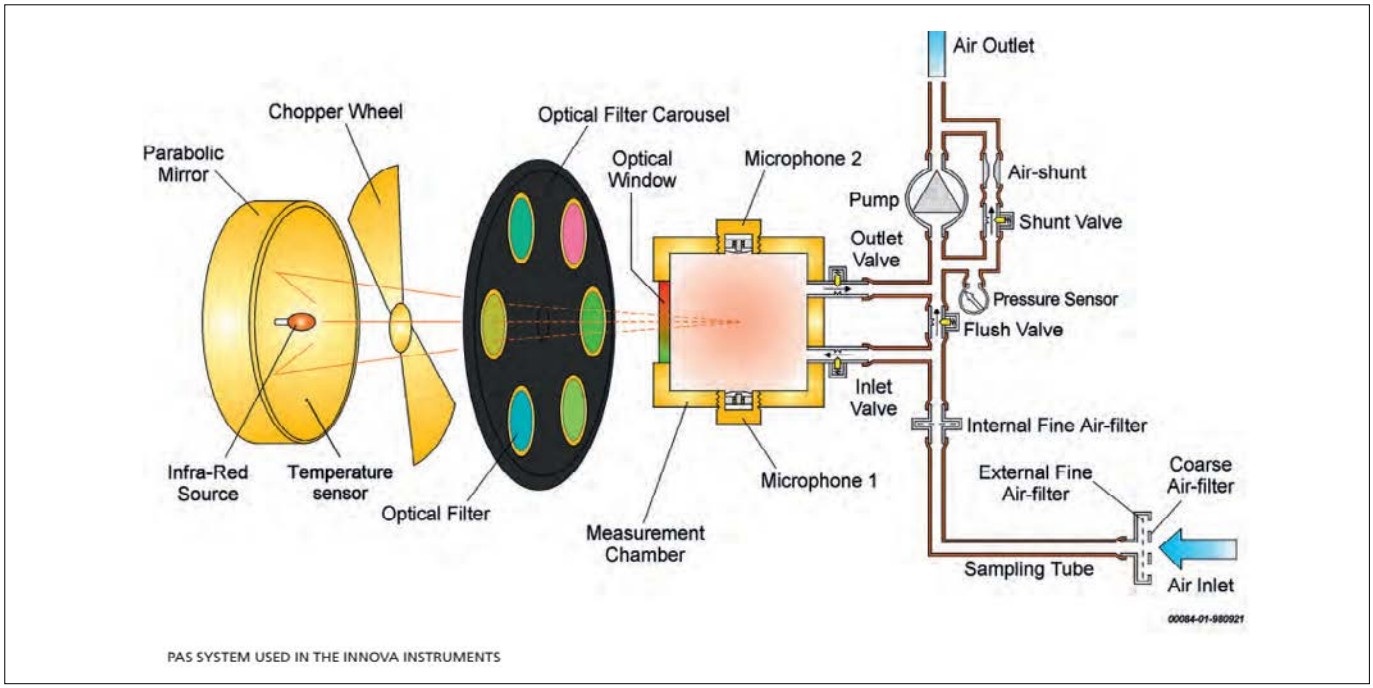


Figure 4. Typical PAS system for DGA measurement as designed by INNOVA

Difficulties with classical PAS application in dissolved gas analysis for power transformers [5]

The applicative purpose of PAS for DGA is more challenging than that of other applications

The applicative purpose of PAS for DGA is more challenging than that of other applications. The DGA measurement involves a preliminary gas extraction. The composition of gases is unknown in most cases, and the measurement environment is noisy and harsh. A partial list of cited and personally experienced challenges can be found below:

1. Oil leaks due to external oil circulation using mechanical pumps and mechanical pump failures, as seen in Figure 4. Almost half of the repairs in PAS-based systems are due to these issues [5].

2. Air serves as the carrier gas to detect gas concentrations dissolved in oil. Typically, air contains trace impurities that can affect gas detection accuracy, making the maintenance of air filters crucial or making it a necessity to use a source of synthetic air as carrier gas, as seen in Table 1.

3. The performance of PAS gas detection systems is intrinsically linked to the sensitivity of the acoustic sensor. Over time, advancements have led to the replacement of traditional microphones with highly sensitive quartz tuning forks, and microcantilever beams as acoustic sensors, enhancing the overall sensitivity and effectiveness of the systems.

4. The results based on [10] showed that the absorption coefficients of acetylene C_2H_2 showed a decreasing trend with the increase of temperature, and the absorption coefficients of the C_2H_2 showed an increasing trend with the increase of pressure, and the effect of temperature on it is much greater than the effect of pressure on it, on this basis, the experimental conditions for the subsequent experiments were determined.

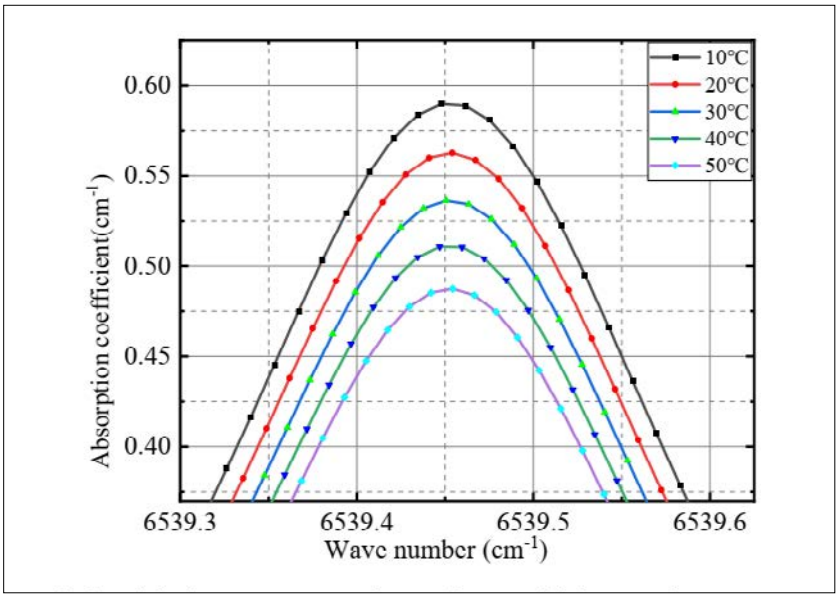


Figure 5. Relationship between C_2H_2 absorption coefficient and temperature [10]

When the PAS is used, the contribution of each gas to the total spectrum is determined by a complex mathematical relationship

5. Vibration and stabilization of the PAS monitor. The PAS measurement is based on very sensitive and delicate pressure variations. External vibration sources may be related to positive false in extreme cases.

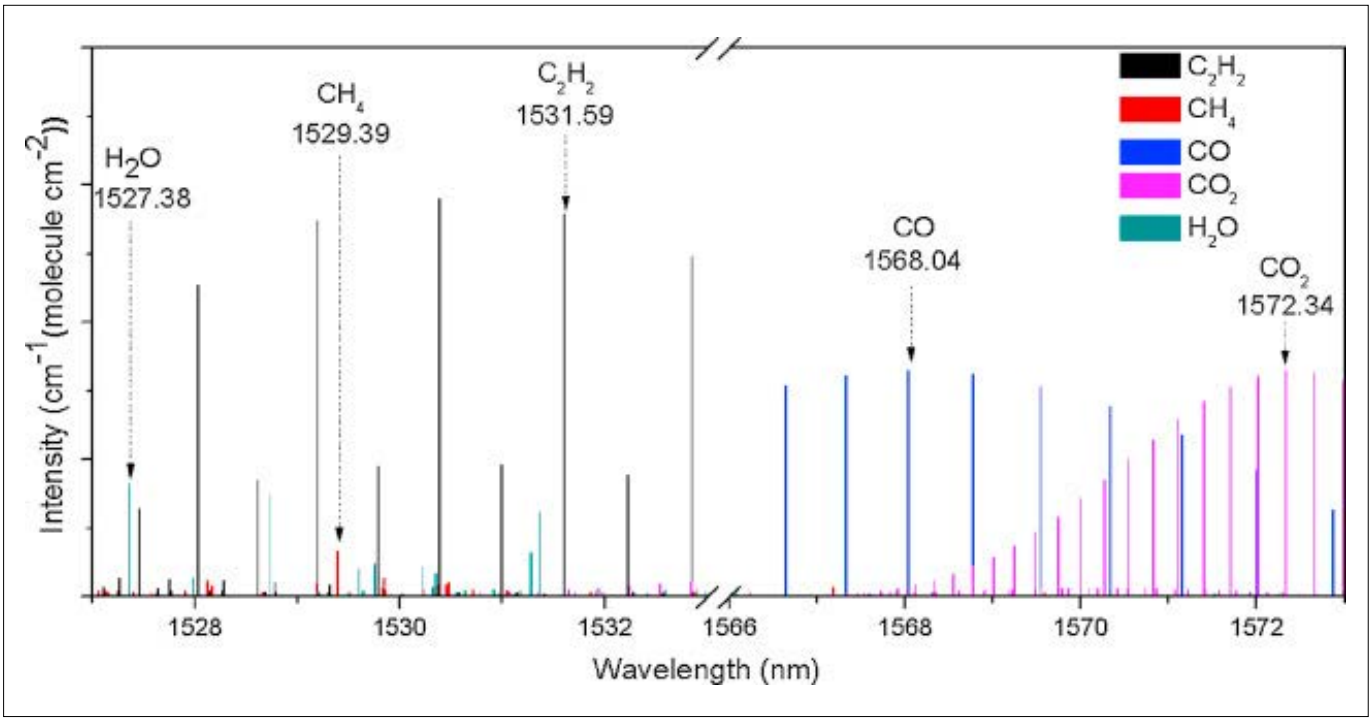


Figure 6a. Description of spectra of a few gases measured by DGA from [11]

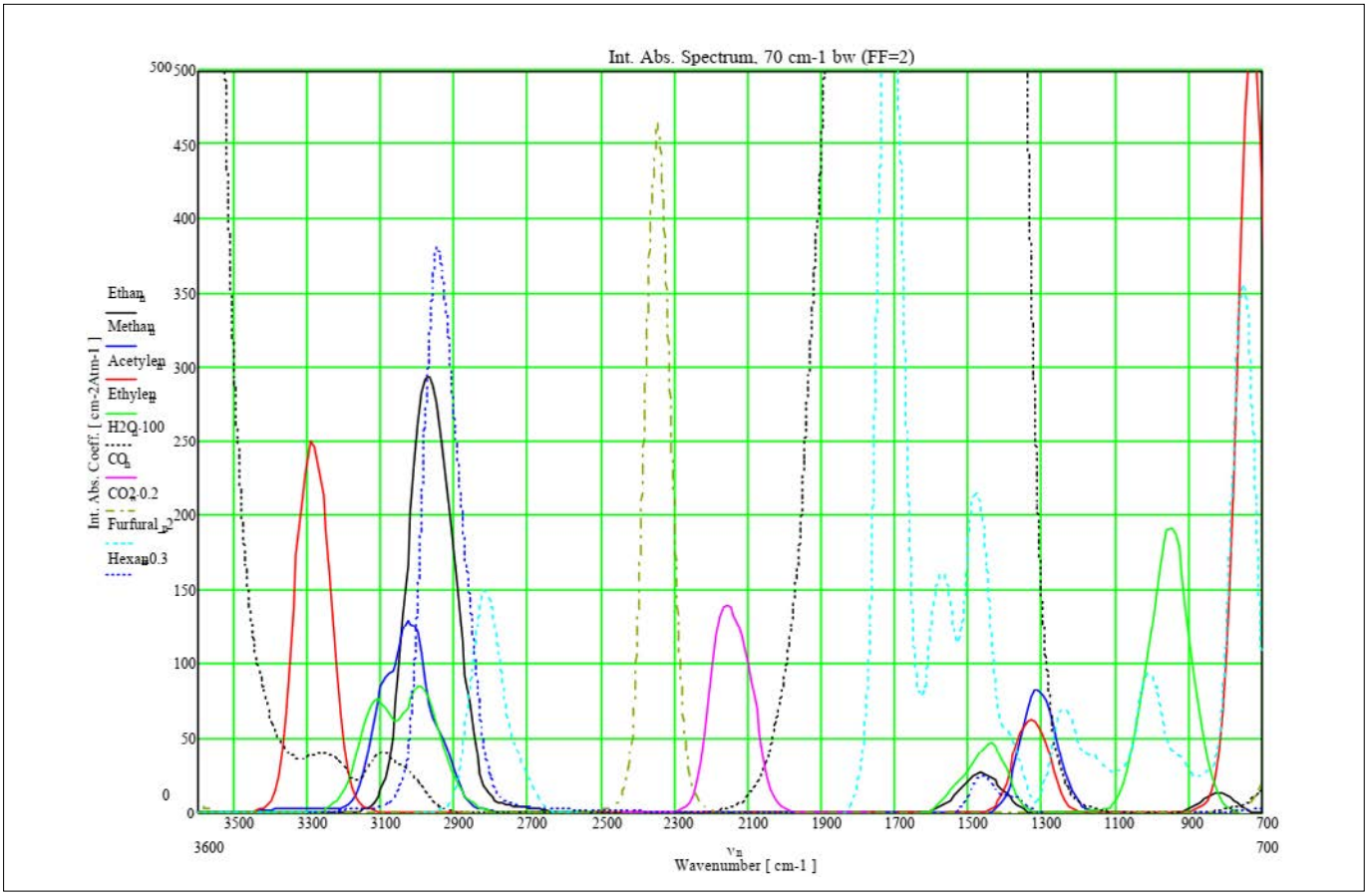


Figure 6b. Early spectra of IR from [13]

6. Dependence of the results from the type of optical filter. As in Figure 4, the filters need to be very fixed and stable to provide the most accurate wavelength for exciting the intended molecular species and avoid interference from known and unknown ones.

7. Dependence of the accuracy from external gas pressure, light, and temperature. The PAS online or portable device may operate at different locations at different altitudes and in different weather conditions. Without dedicated devices, it is impossible to preserve constant atmospheric pressure. This parameter may affect the response factor for DGA measurements.

8. Cross-interference of wavelengths between various gases, including water vapour, which makes it difficult to identify gases, see Figure 6.

Table 1. Comparison of PAS results with other dissolved gas measurements and gas-in-oil standards (hydrogen not measured by PAS)

		H_2*	CO_2	C_2H_2	C_2H_4	C_2H_6	CH_4	CO
air	n	19	19	19	19	19	19	19
	std%	14	7	12	6	10	9	11
	std	7.7	199.4	0.7	48.9	17.2	67.3	84.5
	avg	53.9	2827.8	6.1	774.7	180.6	733.5	759.8
artificial air	n	19	19	19	19	19	19	19
	std%	13	8	9	2	2	7	10
	std	8	267	1	17	3	54	85
		67	3303	6	794	193	792	864

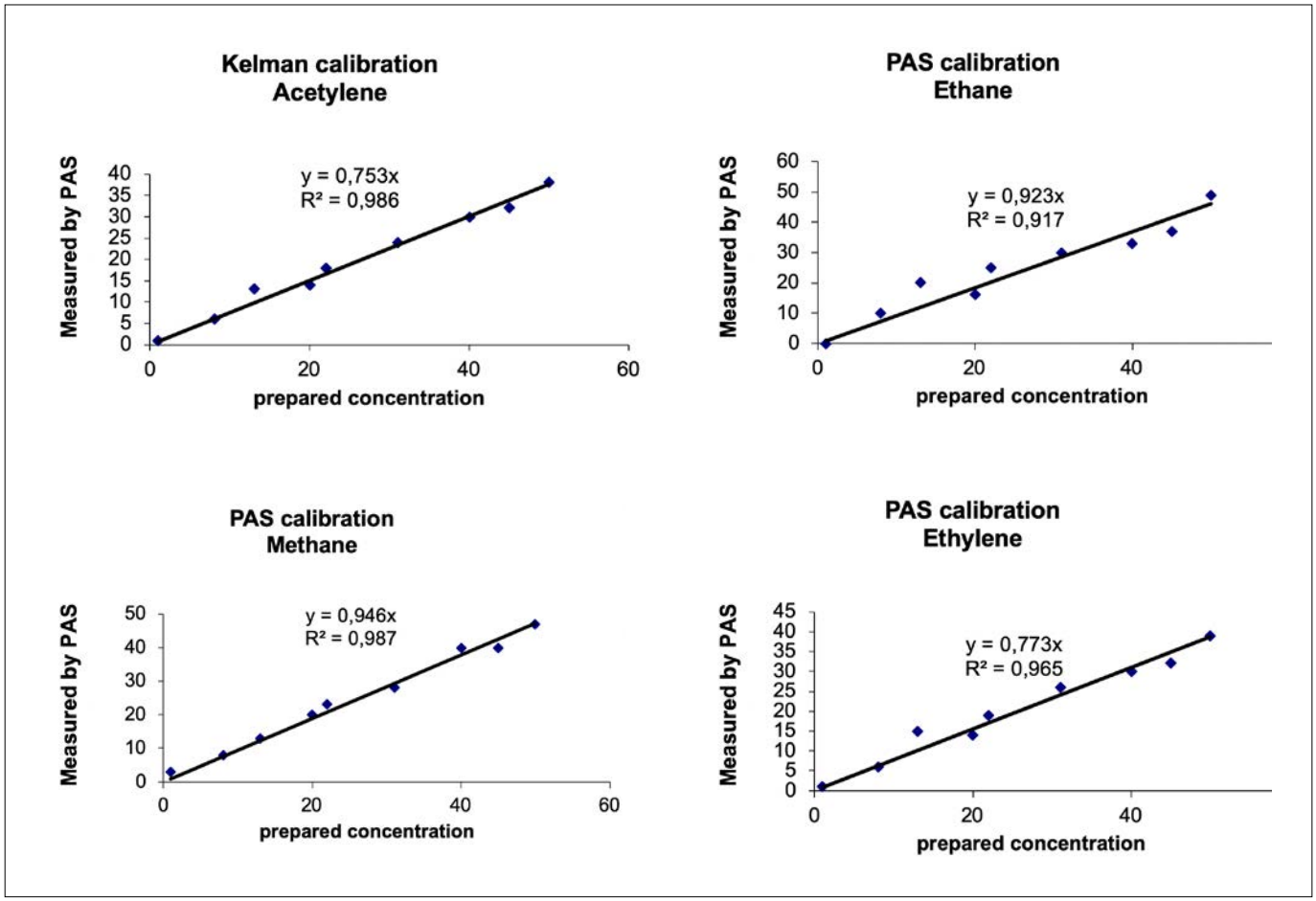


Figure 7. Calibration with a gas-in-oil mixture of an old version of the PAS device

9. Correlation between gas measurement of some PAS devices with standardized prepared gas-in-oil mixture, see figure 6. For methane, the correlation is 1 to 1, but for acetylene, it is 1 to 0.75. It is important to test all the gases' response factors.

10. The average of 5 PAS device measurements of gas-in-oil standards 100 PPM and 500 PPM is comparable with measurements by standardized gas chromatograph calibrated by multiple gas-in-oil in-house mixtures. The relative standard deviation RSD% is higher than IEC60567 requirements, shown in Tables 2 and 3.

11. In comparison between online GC and online PAS versus laboratory-calibrated GC, the online GC seems to be more accurate in this case than online PAS.

12. Photoacoustic Spectroscopy (PAS) struggles to detect oxygen (O_2) and nitrogen (N_2) because these gases do not have strong absorption bands in the infrared spectrum, which PAS typically utilizes. Both O_2 and N_2 are homonuclear diatomic molecules without a permanent dipole moment, necessary for IR absorption. Consequently, they do not produce a significant photoacoustic signal. For measuring these gases, alternative methods like paramagnetic sensors for oxygen and thermal conductivity sensors for nitrogen are more effective and commonly used due to their ability to detect the unique physical properties of each gas.

13. The contribution of each gas to the total spectrum is determined by a complex mathematical relationship.

Table 2. Comparison of the output of 5 PAS devices of 100 PPM gas-in-oil standard versus GC-HS (hydrogen not measured by PAS)

	True North 100 PPM	Standard DGA by Gas Chromatograph -Head space IEC-60567, Headspace calibrated with multiple gas-in-oil mixture	An average of 5 Photoacoustic devices	RSD% of 5 Photoacoustic devices
Hydrogen (H_2)	98	93	96*	29*
Carbon Dioxide (CO_2)	130	147	167	74
Carbon Monoxide (CO)	102	101	105	28
Ethylene (C_2H_4)	101	99	120	20
Ethane (C_2H_6)	101	100	133	17
Methane (CH_4)	102	99	114	24
Acetylene (C_2H_2)	100	97	89	23
Total combustion dissolved gases	604	589	657	22

Table 3. Comparison of the output of 5 PAS devices of 500 PPM gas-in-oil standard versus GC-HS (hydrogen not measured by PAS)

	True North 500 PPM	Standard DGA by Gas Chromatograph: Head space	An average of 5 Photoacoustic devices	RSD% of 5 Photoacoustic devices
Hydrogen (H_2)	491	491	464	27
Carbon Dioxide (CO_2)	531	502	598	19
Carbon Monoxide (CO)	514	534	485	26
Ethylene (C_2H_4)	505	485	525	20
Ethane (C_2H_6)	508	488	572	17
Methane (CH_4)	526	501	496	24
Acetylene (C_2H_2)	495	483	407	21
Total combustion dissolved gases	3039	2982	2947	22

Table 4. Comparison of the output of online PAS devices versus GC-HS and versus online GC (hydrogen not measured by PAS)

	Standard DGA by Gas Chromatograph -Head space	DGA by Online gas chromatograph	Online PAS	Relative difference: PAS and GC online %
Hydrogen (H_2)	390	378	155	59
Carbon Dioxide (CO_2)	1515	2460	2247	9
Carbon Monoxide (CO)	304	420	349	17
Ethylene (C_2H_4)	3396	3200	3355	5
Ethane (C_2H_6)	539	554	680	23
Methane (CH_4)	2471	2480	2230	10
Acetylene (C_2H_2)	19	17.8	14	21
Total combustion dissolved gases	7119	7050	5244	26

Table 5. Comparison of relative error of 5 PAS devices versus GC-HS when measuring 2 levels of gas-in-oil standards 100 & 500 PPM (hydrogen not measured by PAS)

	Relative error for DGA by GC-HS when measuring 2 levels of True North	A relative error average of 5 photoacoustic devices when measuring 2 levels of True North
Hydrogen (H_2)	3%	24%
Carbon Dioxide (CO_2)	9%	73%
Carbon Monoxide (CO)	2%	19%
Ethylene (C_2H_4)	3%	19%
Ethane (C_2H_6)	2%	23%
Methane (CH_4)	4%	20%
Acetylene (C_2H_2)	3%	25%
Total combustion dissolved gases	3%	24%

From the above experimental study, it may be understood that PAS necessitated improvements to be equal to standard gas chromatography performances

From the above experimental study, it may be understood that PAS necessitated improvements to be equal to standard gas chromatography performances.

Those insights have also been expressed by different publications in recent years [6, 8-10, 12].

The two main areas for such improvements that were recently studied and performed were the source of energy to excite the target molecules, replacing the IR lamp coupled with the colour filter by a specific laser with discrete, stable, and accurate energy. The two primary sources for generating the photoacoustic effect in PAS are lasers (Laser PAS) and infrared light sources (IR PAS). A few considerations should be made when using light sources and special sound-sensing devices.

Laser PAS (Laser photoacoustic spectroscopy)

The arrangement of laser to PAS for DGA was first mentioned in literature in 2011 [15]. Since then, the number of papers on this subject has increased, and recently, at least two companies have released commercial gas-in-oil monitors based on laser improvement for DGA.

There are both pros and cons of implementing lasers in PAS technology for DGA.

Pros:

- **High Sensitivity and Selectivity**: Lasers provide a very focused and intense light source, which can enhance the sensitivity and selectivity of the PAS technique for detecting specific gases.
- **Wide Tunable Range**: Many laser systems, especially those using quantum cascade lasers, can be tuned over a wide range of wavelengths, allowing for the detection of multiple gases with specific absorption features.
- **Fast Response Time**: Laser PAS can offer fast response times due to the direct and rapid absorption and subsequent acoustic signal generation.

Cons:

- **Cost**: Lasers, particularly tunable diode lasers or quantum cascade lasers, can be expensive compared to other light sources.
- **Complexity**: Operating and maintaining laser systems may require more technical expertise and sophisticated calibration.
- **Safety Concerns**: Lasers can pose safety risks, such as eye damage, if not properly handled or shielded.

The pros of remaining wit classic IR PAS (Infrared Photoacoustic Spectroscopy) include:

Pros:

- **Cost-Effectiveness:** IR sources are generally less expensive than laser systems, making IR PAS more accessible for routine applications.
- **Simplicity**: IR PAS systems are typically easier to operate and require less maintenance compared to laser-based systems.
- **Broad Coverage**: Broadband IR sources can cover a wide spectral range, which is useful for the simultaneous detection of multiple gases with overlapping absorption bands.

Sensitive sound sensing device: Cantilever-enhanced Photoacoustic Spectroscopy (CEPAS)

To increase the measurement capabilities of PAS for DGA, taking advantage of the Cantilever principle may be applicable. There are both pros and cons of this approach.

Pros:

- **Higher Sensitivity**: The use of a cantilever as a sensitive mechanical sensor in CEPAS allows for the detection of very low concentrations of gases, improving the sensitivity beyond traditional PAS.
- **Minimal Noise Interference**: The cantilever's mechanical resonance enhances the signal and helps distinguish it from background noise, providing cleaner and more reliable results.
- **Broad Gas Coverage**: CEPAS can detect a wide range of gases by adjusting the light source's wavelength, making it versatile for detecting various fault gases in transformers.

Cons:

- **Complex Setup**: The inclusion of a mechanical cantilever system can complicate the setup and calibration of the equipment, requiring more careful handling and maintenance.
- **Cost**: The additional components and technology involved in CEPAS typically make it more expensive than standard PAS setups.
- **Fragility**: The cantilever, being a delicate component, can be prone to damage or misalignment, which could affect the reliability of the **Choosing Between CEPAS and PAS for DGA**

The choice between CEPAS and traditional PAS for DGA depends on specific requirements such as:

- **Sensitivity Needs**: If detecting extremely low concentrations of fault gases is crucial, CEPAS might be the better choice.
- **Budget and Resource Availability**: For organizations with limited budgets or less technical expertise, traditional PAS might be more appropriate.
- **Application Scope**: For comprehensive monitoring where higher sensitivity and minimal noise are critical, CEPAS offers significant advantages.

Conclusion

Photoacoustic spectroscopy (PAS) is a powerful method with applications in many domains of life, such as medicine, space research, the environment, and many others. Since the beginning of the millennium, it has also become a leading technology for dissolved gas analysis. By 2024, most multi-gas DGA measurements were performed using PAS, available in both portable and online devices. From a technological perspective, PAS may replace gas chromatography. However, there are still a few issues that need to be addressed, such as adapting laser technology to excite very specific molecules and developing dedicated acoustic devices to increase measurement sensitivity and lower the detection limit. Given the extensive publications on laser and cantilever applications for DGA, it seems very plausible that PAS will replace GC and other spectroscopy technologies.

Disclaimer: This column is not a recommendation to use spectroscopy technology or any other, for online DGA measurement. Each transformer user should consider the most adequate needs for online DGA, by specific needs, budget and experts' recommendations.

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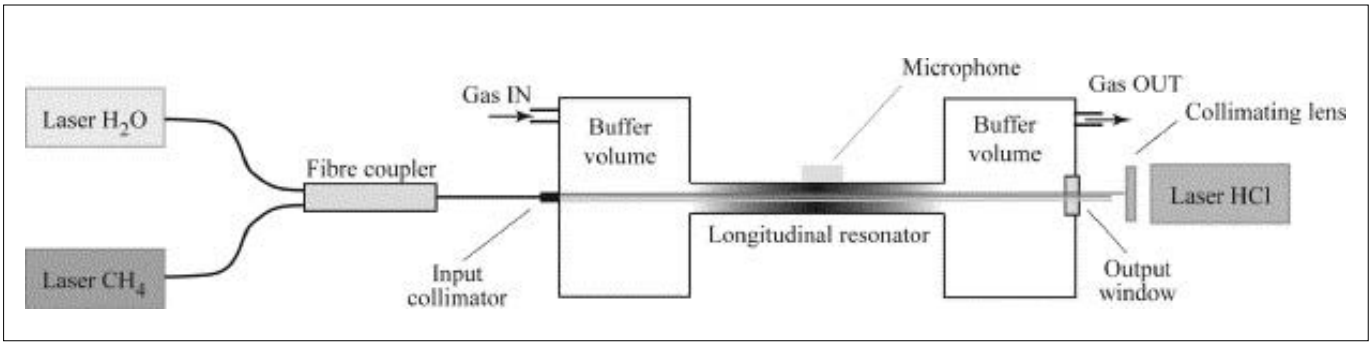

Figure 8. Schematic representation of our experimental setup for the measurement of CH4, H2O and HCl (hydrochloric acid) using three near-infrared DFB lasers and a PA cell operated in its first longitudinal resonance [11]

By 2024, most multi-gas DGA measurements were performed using PAS, available in both portable and on-line devices

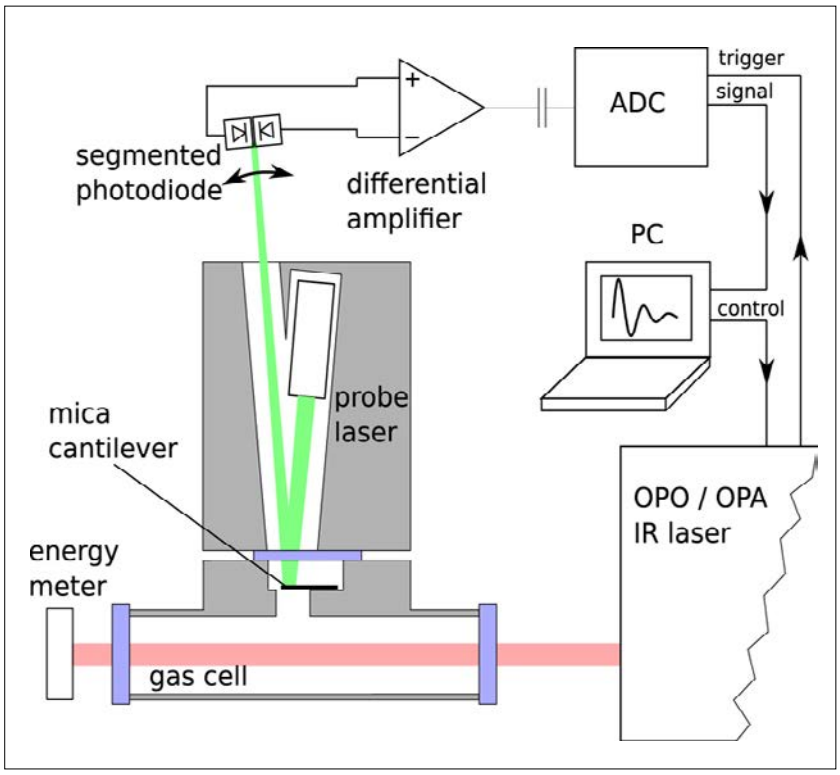

Figure 9. Schematics of the experimental setup for photoacoustic spectroscopy with the cantilever detector. [8]

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