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Review paper

SENSING WITH SOUND: IMPROVING GASES AND SOLID ANALYSIS BY PHOTOACOUSTIC SPECTROSCOPY

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Abstract. *The development of photoacoustic spectroscopy is being driven by the growing demand for precise, efficient, and reliable detection methods that can be used for in situ measurements and real-time monitoring. Along with rapid technological progress, photoacoustic spectroscopy became an ultra-sensitive, selective, cost-effective technique that can meet the demanding requirements for environmental monitoring, industrial safety, and medical diagnostics. This paper highlights how continuous improvements in photoacoustic technologies, including the use of appropriate laser sources as well as sensing elements, and machine learning methods, are pushing the limits of gases and solid analysis and providing critical tools for addressing modern scientific and industrial challenges.*

Key words: *photoacoustic spectroscopy, trace gases analysis, material characterization, photoacoustic imaging, machine learning*

1. INTRODUCTION

To meet the evolving demands for detecting and monitoring of a variety of phenomena regarding environmental pollution and climate change, industrial process control and workplace safety, agriculture and food industry, as well as medical diagnostic, modern detection techniques should fulfill very stringent criteria. Greenhouse gases, ozone, and toxic and flammable gases, known as trace gases, usually have concentrations in the range

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of ppm (parts per million)[1]. Traditionally, non-optical and optical methods have been used for concentration measurement. Non-optical methods (chromatography and mass spectrometry) regardless of high sensitivity, can be time-demanding and inappropriate for real time and field measurements or can suffer from stability and sensitivity (electrochemical and semiconductor sensors). Optical gas sensing methods stand out as highly sensitive and selective, with fast response time, allowing real time in situ measurement.

Over the years, photoacoustic spectroscopy (PAS) as an optical, laser-based detection technique, has evolved into a powerful, highly sensitive (from ppm to ppt range of concentration), selective, robust, cost-effective, and easy handling technique with large dynamic range (several orders of magnitude in concentration) [1].

PAS combines optical and acoustic phenomena, converting optical into acoustic energy. Photoacoustic (PA) effect occurs when a sample (gas, liquid, or solid) absorbs modulated or pulsed laser radiation. Localized sample heating led to generations of pressure (acoustic) waves, which are typically detected by appropriate detectors (usually microphones). PAS enables non-invasive, sensitive investigations of samples. Along with rapid technological progress and the development of lasers and sensors, PAS has been recognized as impactful in many areas: trace gas detection, industrial process control, chemical reaction dynamics, monitoring of deexcitation processes, investigation of thermoelastic and other physical properties of materials, acoustic-electronic properties of semiconductors, medical imaging, human breath diagnosis, and many others. This paper provides a brief review of some modern PA applications in gaseous, solid sample analysis, and medical diagnostics, to highlight the versatility and huge potential of PA application. Also, a review of some machine learning implementations in PAS analysis has been given.

Trace gas detection by PAS offers multi-component and real-time, in situ detection with no need for sample preparation. Industrial applications of PAS provide continuous monitoring and detection of toxic, flammable gases, hazardous gas leaks, emissions control and workplace safety. PA technique is suitable for the study of thermal and optical characterization of a wide range of liquids (from optically transparent to opaque), measurement of pollutant concentration, etc. Material characterization by PAS provides detailed insights into mechanical, thermal, and structural properties. The propagation of PA waves is influenced by the material's characteristics, allowing precise analysis of its physical features [2]. This technique is especially beneficial for opaque, nontransparent materials where traditional optical methods are not applicable. Novel PAS applications are focused on medical diagnostics, offering non-invasive, non-ionization accurate, and fast analysis [3]. Photoacoustic imaging (PAI) is used to visualize the mechanical and optical properties of soft tissues. Utilizing the acoustic waves generated by light absorption in tissues, PAI provides high-resolution images of biological structures.

2. Trace Gases Analysis by Photoacoustics

The PA effect was discovered by Alexander Graham Bell in 1880. He found that a solid sample can generate sound when it is illuminated by an interrupted beam of sunlight. The discovery was neglected for years due to the lack of suitable light sources and detectors. After the laser invention, PA effect has sparked a keen interest and its widespread use has started. The high spectral brightness of the laser, and appropriate techniques for acoustic

[1] Concentrations are expressed as parts per million 10^6 (ppm), billion 10^9 (ppb) or trillion 10^{12} (ppt), by volume.

signal amplification enable the determination of low concentrations of air pollutants. Inspired by the encouraging results of Kreutzer's measurements of methane (CH_4) concentration in the ppb range (1971.), many researchers started to apply PAS in various scientific fields [4].

A PA signal is generated by the absorption of laser radiation in a sample. To achieve high sensitivity in trace gas detection, laser radiation must coincide with the absorption lines of the measured gas species. Photon energy in the infrared (IR) spectral region (called molecular fingerprint region, from 3 to 12 µm), excited molecule's rotational and vibrational energy state. Absorbed energy release via molecule collisions. The fastest relaxation type of absorbed IR energy is transfer from vibrational to translational modes of colliding molecules (V-T relaxation). Energy is released via V-T relaxation type heating the sample. Localized heat increasing the temperature causes pressure to rise. Since laser excitation can be continuous (modulated) and pulse, temperature and pressure vary periodically generating thermal and acoustic waves (Fig. 1).

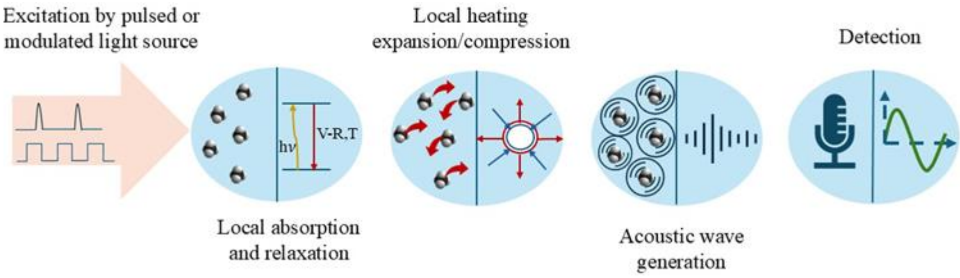

Fig. 1 Typical scheme for PA wave generation in a gas sample

Experimental arrangement for PAS measurement typically consists of a laser as a light source, a PA cell (for signal generation) and a detector (pressure sensing devices for sound detection). The commonly used light source in trace gas measurement is a laser with a narrow bandwidth, and wavelength that matches the absorption lines of investigated molecule species. PAS is an appropriate technique for trace gas concentration measurement, due to the proportionality between the intensity of the PA signal, absorbed energy and concentration of absorbing species [1,5]. This proportionality is valid for a wide range of concentration, (ranging from high concentrations in urban to small concentrations in rural environments). High-power lasers (CO_2, and CO lasers) are preferred sources in trace gas measurements, providing high sensitivity (in the sub-ppb range) and high selectivity. They are mainly used for laboratory experiments due to their cumbersomeness and complexity. Nowadays, more compact and appropriate forms for in situ measurements are available. In various areas of PAS application, different laser sources have been applied: diode laser, quantum cascade laser, Nd: YAG laser, light-emitting diode (increasingly used in PA applications in medicine), and many others.

The sensitivity of PA detection depends on the sensitivity of acoustic detectors, geometry and design of PA cells. Depending on operation (at an acoustic resonance or not) the PA cell can be described as resonant or nonresonant [5]. Sound waves in PA cells are detected by microphones (capacitive microphones are the widely used microphones for sound detection). To enhance the sensitivity of PA measurement and signal-to-noise ratio, different modifications of typical PAS arrangement have been designed.

To advance detection of trace gases by PAS quartz-enhanced photoacoustic spectroscopy (QEPAS) has been proposed [6]. The sensing element in the QEPAS setup is a quartz tuning fork (QTF), an efficient acoustic resonator that increases weak PA signals. QTF effectiveness has been proved in the detection of numerous gases at concentrations ranging from ppm to ppt. A recent review by Sampaolo et al. [6], emphasizes QEPAS's versatility in multi-gas detection including CH_4, nitrous oxide (N_2O), and carbon monoxide (CO). De Palo et al. [7] proposed QEPAS for the detection of eight air pollutants (CH_4, N_2O, CO, nitrogen dioxide - NO_2, carbon dioxide - CO_2, nitric oxide - NO, sulfur dioxide SO_2, and ammonia - NH_3), in the ppb concentration range underlining its ability for urban air quality monitoring. Lin et al. [8] introduced an all-optical off-beam QEPAS spectrophone based on double-pass acoustic microresonators, demonstrating advanced detection efficiency of CH_4 (2.41 ppm), and applicability in harsh environments and under strong electromagnetic interference. To achieve sub-ppb detection (of 54 ppt) of NO_2 (which is essential for controlling ozone formation), Yin et al. [9] developed a PA system with a differential PA cell and multimode diode laser. Further applications of QEPAS are explored in methane-based gas leaks, demonstrating hydrogen sulfide (H_2S) detection (of 2.5 ppm) in mixed gas environments [10]. The simultaneous detection of pollutants with overlapping spectra such as H_2S and CH_4 (from oil wells and refineries) is of key importance, due to potential environmental and health risks. A portable QEPAS sensor for real-time CO monitoring in urban areas, developed by Sgobba et al. [11] highlights the field-deployment potential of modern PAS systems. Zheng et al. [12] utilized near-IR telecommunication diode lasers for CO_2 detection in atmospheric conditions. A wide dynamic range of PAS detection of several orders of magnitude is an especially important feature for long-time monitoring in the chemical industry, warfare agents and explosives. For example, atmospheric NH_3 concentrations can range from a few ppb to hundreds of ppb in polluted areas, and up to hundreds of ppm in industrial plants following leaks [13].

Trace gas detection of volatile organic compounds (VOCs) emitted mainly from transportation, engine exhaust, and refineries, including benzene, toluene, ethylbenzene, and xylene, are of great importance due to their health impact, even at ppb levels. Advanced methods for detecting VOCs using long-wavelength quantum cascade lasers have been investigated by Kinjalk et al. [14]. Further improvement of PAS sensitivity (more than one order of magnitude) is achieved using a micromechanical cantilever as a sensing element in the cantilever-enhanced PAS proposed in [15].

The main advantages of PAS are adaptability and the capability to satisfy specific measurement requirements for sensitive and selective detection of various gas species, by replacing laser source, cell or sensing element with a suitable one.

3. Material Characterization by Photoacoustics

The underlying mechanism of PA generation in solid and liquid samples has some common characteristics. The dominant mechanism of PA wave generation in liquids is thermoelastic mechanisms. Laser radiation heated a limited volume of liquid causing a temperature gradient which leads to the strain and PA wave formation. Using this mechanism, the optical and thermal properties of liquids can be measured, Also, flow speed and liquid viscosity measurement by PA technique are very important in medical diagnostics.

PA signal in a solid sample is created after complex thermomechanical processes. As a result, the PA signal provides valuable information of the thermal, optical, and elastic characteristics of the sample. Accordingly, the PA technique has been widely applied for the study of sound velocity, temperature, thermal diffusivity, thermal conductivity elasticity, flow velocity, specific heat, thickness, subsurface defects, material discontinuities, crystallinity, phase transition and many others [2]. Nowadays, along with the rapid development of renewable and sustainable energy technologies, thermal conductivity and diffusivity measurements are crucial for the selection of materials that can be used in thermoelectric energy conversion, thermal energy storage, sensors, etc. Some applications require materials with low thermal conductivity (to minimize heat leakage), while other high thermal conductivity is needed to enhance heat transfer and energy efficiency [16]. Measurements of the thermal properties of materials, especially those with nanoscale dimensions (e.g., thin films, nanowires), are very demanding. PAS is a contactless, non-destructive technique, applicable for in situ measurement. The PA method has proved to be very successful for the study of totally opaque materials, and light scattering materials (powders), where conventional spectroscopy is not usable or provides inadequate results.

PA signals can be generated directly in a sample that absorbs light energy. Otherwise, it is generated indirectly within a medium adjacent to the sample, such as a solid-gas-microphone configuration (mostly used in the thermal, optical and mechanical study of solids). After absorption of electromagnetic energy, thermal diffusion takes place, leading to elastic stress as a result of thermal expansion. Theoretical explanation of PA signal generation in solids was developed by Rosencwaig and Gersho [17] and extended by McDonald and Wetsel which include thermally induced mechanical vibration of the sample surface [18]. Based on the underlying processes of the PA generation, two components can be distinguished: a thermodiffusion (caused by thermal diffusion mechanism dominating at a low frequency), and thermoelastic (caused by thermoelastic expansion and bending, dominating at high frequency). In semiconductors, the PA signal has an additional plasmaelastic component (originates from mechanical strain due to carrier recombination) [19]. Important information about the thermophysical and optical characteristics of the sample can be obtained by analyzing PA signal amplitude and phase dependency on frequency [20]. Thermal conductivity and diffusivity are important characteristics of semiconductors, polymers, ceramics, and composites. Also, PA can be used to evaluate the elastic properties of a material, especially in thin films [21,22,23]. Acoustic waves generated by the PA effect carry information about the thickness of each layer and any imperfections at the interfaces. This makes PA ideal for characterizing materials in microelectronics and coatings [24]. PA technique has been applied in determining the reflection coefficient and thermal diffusivity of a specific metal mirror, characterized by high reflection coefficient [25].

The possibility to develop a PA experimental setup according to specific measurement requirements is a considerable advantage of the PA technique (open or closed PA system configuration, depending on sample properties to be measured) [21,22,23]. Commonly used acoustic detectors are microphones for pressure variation detection (condenser or electret microphone) or piezoelectric devices more suitable for PA detection in solids. Although there are many different sensors for PA detection such as fiber optics, electromagnetic acoustic transducers, the Michelson interferometric system, etc. Also, PA configuration for solids can be adjusted to in situ measurements [26].

It is interesting to note that PAS can play a significant role in fundamental research in physics. Extremely fast relaxation phenomena and nonequilibrium processes have not been well described up until now, because orders of magnitude for relaxation times of various subsystems in condensed matter are unknown (even approximately). The theoretical prediction ranges from 10^{-14} s (for metals and superconductors) to 10 s (for biological tissues) [27]. According to theoretical predictions in complex systems such as noncrystalline solids, polymeric materials, or biological tissues, the influence of these relaxations could be expected in simple experimental setups, while, in crystals and 2D crystals relaxations impact could be expected in the nanosecond range or shorter. The development of modern detectors, ultra-fast electronics, pico- and attosecond lasers have accelerated the enhancement of experimental PAS setups which could detect relaxation phenomena even in highly ordered interior structures of condensed matter. However, one of the obstacles to characterizing relaxation phenomena by PAS or other methods is the lack of a theoretical model which is essential for the analysis and interpretation of experimental results. Most models of PAS signals are based on classical Fourier heat conduction theory, which is inherently approximative and established at the phenomenological constitutive relation (Fourier's constitutive relation) [28]. Nowadays, in scientific literature for modeling PAS signals generalized theories of heat conduction have been increasingly used: from hyperbolic theories [29,30,31,32], and the dual-phase lag theory [33], to fractional theories of anomalous diffusion [34,35,36]. Using a highly sophisticated PAS experimental setup and the hyperbolic heat conduction theory thermal relaxation time (in the nanosecond range) is measured in 2D graphene lattice at temperatures above 100 K and 200 K [37, 38].

4. Medical Application of Photoacoustics

PAS has been used as a promising tool in a various medical application: qualitative and quantitative analysis of pharmaceutical drugs, human breath diagnosis, breast cancer diagnosis, detection of cardiovascular disease, blood oxygenation levels monitoring, and others. The medical use of the PA technique is mainly focused on photoacoustic imaging (PAI) [3,39,40]. Imaging biological tissues plays a crucial role in diagnostics of diseases. Commonly used techniques include magnetic resonance imaging (MRI), X-ray computed tomography (CT), and positron emission tomography (PET). While these techniques are widely used, they have drawbacks such as potential health risks from ionizing radiation, limited mobility, and high costs. In contrast, PAI offers a noninvasive, nonionizing alternative, leveraging the PA effect. In PAI short laser pulses (in the nanosecond range) irradiate biological tissues whose components absorb photons, and subsequent localized heating and thermoelastic expansion occur. This process generates megahertz-range ultrasound (US) waves that can be detected and used to reconstruct images. PAI stands out because of its ability to provide high-resolution and deep-tissue imaging, outperforming purely optical techniques, which suffer from significant scattering with increasing depth. Compared to optical scattering in soft tissues, which greatly reduces spatial resolution with depth, US scattering in biological tissues is two to three orders of magnitude weaker, allowing clearer imaging at greater depths [41]. However, PA wave propagation is influenced by both scattering and absorption within the tissue, and attenuation varies based on tissue type and frequency. PA signal is determined by energy deposited in a tissue, scattering characteristics, thermal properties (thermal diffusivity and thermal expansion coefficient), and the elastic features of the tissue.

Frequently used excitation source in PAI is a pulsed Q-switched Nd: YAG laser. Recently, more economical, low-cost laser sources such as laser diode and LED have been used as suitable for portable PA sensing and imaging systems [42,39]. PA signals are detected by a US sensor placed around the sample surface [39]. The commonly used sensor for US detection is piezoelectric crystal, which converts pressure change to an electrical signal. Also, optical detectors with wide bandwidth can be used for sensitive US detection. Numerous novel technical solutions of PA are developed into various imaging modalities [39]. PA signal analysis can generally be performed in both the time and frequency domains. In the time domain, key characteristics of the sample - such as optical absorption, absorber position, and absorber size - can be inferred from four main parameters of the PA signal: amplitude, time delay, signal width, and relaxation time. Different optical absorption properties between normal and pathological tissues result in variations in PA signal amplitude, providing high contrast and aiding in tissue differentiation. The time delay offers critical information about the depth of the absorber and, together with the PA signal, is crucial for accurate image reconstruction [3]. Various algorithms have been developed to solve inverse problems in PA image reconstruction (backpropagation, iterative reconstruction methods, and others) [40,41]. The choice of algorithm is the trade-off between image reconstruction accuracy and computational efficiency. To improve PAI contrast and sensitivity, reference [43] suggests using plasmonic hetero-nanoparticle with broadband transient responses and wavelength tunability, for precise control of light absorption and heat conversion. Those characteristics could be crucial for high-resolution imaging applications in biomedical imaging and diagnostics.

Unlike traditional US diagnostics, PAI provides valuable information about tissue composition by exploiting the wavelength-dependent absorption of optical energy. Tissue chromophores - such as hemoglobin, lipids, proteins, water, and melanin - absorb light at specific wavelengths, which enables targeted imaging for various medical conditions. By selecting appropriate excitation wavelengths, PAI enhances the detection and diagnosis of cancers and hematological disorders. Major biomedical applications of PAI include brain imaging, arthritis detection, arterial plaque identification, and diagnostics for hematological diseases and cancers [39].

Human breath analysis represents another important medical application of the PA technique. It has been established that many exhaled compounds can reflect both physiological and pathophysiological states, offering diagnosis of various diseases [44]. Compounds such as NH_3, NO, H_2S, and VOCs are byproducts of normal metabolism, while others may be caused by different reasons. PA sensing offers a noninvasive, real-time, sensitive detection in the ppm to ppb range [44,45]. Additionally, using the PA technique for breath analysis it is possible to detect bacterial infections [45].

5. Intelligent Photoacoustics

In the realm of PA analysis, one of the key challenges is the inverse problem - reconstructing the physical properties of a sample, such as gas concentration, material and tissue characteristics, from the measured PA signals [46]. The complexities of PA analysis, including multiparameter function, nonlinearity, and noise, along with the need for real-time processing, pattern recognition, classification, and optimization, make AI and machine learning - ML (as a subcategory of AI) a highly suitable tool for PA applications. AI's adaptability allows it to handle nonlinear, ill-defined, incomplete, and noisy data while offering rapid signal processing, real-time operation, and high accuracy and sensitivity.

In trace gas analysis, the complexity of multi-gas mixtures, potential interferences between components, noise, and variations in experimental parameters often affect the precision of PA detection. The generated PA signal depends on numerous factors, including the sample's absorption properties, laser parameters (wavelength, modulation frequency, fluence), detector characteristics, temperature, pressure, and others. Variations in these parameters during experiments can influence the PA signal. Solving the inverse problem by extracting gas sample characteristics (such as concentration, relaxation time, and optical absorption coefficient) and experimental parameters (such as the spatial profile of the laser beam) have traditionally relied on algorithms that are time-consuming and sensitive to initial parameter selection [47,48]. Artificial neural networks (ANNs), highly parallel connectionist systems, offer a faster alternative, enabling real-time analysis by processing data more efficiently than traditional methods. As adaptive systems, ML algorithms improve performance over time, refining estimations and accuracy without relying on exact mathematical models. ANNs have been successfully applied for simultaneous estimation of PA signal parameters, such as the spatial profile of the laser beam and the V-T relaxation time of molecular species [49]. Real-time, and accurate estimation of parameters by ANNs allows correction of laser parameter variations during experiments, preventing overlaps in absorption efficiencies among different gases.

To address fluence variation based on PA signal analysis, Lukic et al. applied another technique designed for dealing with imprecise or fuzzy data: the adaptive-network-based fuzzy inference system (ANFIS) [50]. In practical applications of PAS for trace gas analysis, an optimization procedure is required to calibrate and fit the measured PA spectrum with a reference spectrum. As an effective method for function optimization metaheuristic algorithms have been applied to resolve challenges in determining optimal values and multiple PA signal parameters. The effectiveness of several metaheuristic algorithms including genetic algorithms (GA), particle swarm optimization (PSO), artificial bee colony (ABC), and simulated annealing (SA) in simultaneous determination of PA signal parameters has been compared in studies [51,52].

In material characterization, ML can be applied to solve inverse problems and predict key mechanical, thermal, and optical properties, thereby facilitating the characterization of complex materials, composites, semiconductors, and thin layers. ML-driven models can handle large datasets in real time, making the characterization process faster and more efficient. Semiconductors and thin layers, which play a crucial role in modern advanced electronic devices, particularly benefit from such approaches. Djordjevic et al. employed ANNs to simultaneously determine thermal diffusivity, thermal expansion coefficient, and thickness from the transmission and frequency-modulated PA response of a sample. Their results demonstrate that ANNs are an effective tool for the precise, real-time characterization of plasma-thick semiconductors [53]. In related work [54,55], researchers applied ANNs to characterize the thermoelastic and geometric properties of aluminum and thin aluminum samples, crucial for applications in thin films, micro- and nanostructures, polymers, and composite materials. Further studies have shown that ANNs are highly effective in estimating the thermal, elastic, and geometric properties of a thin TiO_2 film deposited on a silicon substrate [56]. ANNs combined with reverse-back procedures for analyzing the optical properties of semiconductors (such as absorption coefficient and reflection) enable the detection of light source variations and changes in the sample surface, as discussed in [57]. Additionally, ANNs can be trained to recognize microphone characteristics, preventing PA signal distortion during measurements [58].

PAI combines optical and ultrasound characteristics to provide high-resolution, spatially resolved images of optical tissue properties. However, determining key tissue parameters requires solving inverse image reconstruction problems. Traditional iterative techniques for solving inverse problems are computationally costly and sensitive to the selection of initial parameters. To address these challenges, ML-powered image reconstruction algorithms, such as deep learning (DL), have been developed to enhance the spatial resolution and contrast of PA images. These algorithms learn from large datasets of medical images, enabling them to improve image quality even in difficult conditions, such as deep tissue imaging, where signal attenuation occurs. DL models can enhance image clarity, improving the visualization of small anatomical structures and early disease markers, such as tumors or vascular abnormalities [59,60]. For diagnostic purposes, ML, particularly DL techniques like convolutional neural networks (CNNs), can automatically segment and classify PA images, distinguishing between healthy and pathological tissues. This is particularly useful in oncology, where ML can aid in tumor detection and monitor disease progression. Moreover, ML algorithms can predict physiological parameters, such as blood oxygenation and hemoglobin concentration, from PA signals, contributing to non-invasive diagnostic assessments [55].

The successful application of ML techniques relies heavily on the availability of valid and extensive training data that accurately represents the problem at hand. Collecting such representative data often requires numerous experiments, which can be challenging and time-consuming. Additionally, neural network limitations can be slow and demanding training processes and the selection of appropriate datasets for training. Choosing the optimal network topology can also be demanding. On the other hand, metaheuristic methods are robust and reliable, capable of exploring a wide solution space and effectively handling noisy data. However, they also have their own limitations, such as the need to adapt to specific problems and the requirement for parameter tuning to achieve optimal results.

6. Conclusion

The growing applications of the PA technique in gas sensing, material characterization, and medical diagnostics highlight its significant potential as a versatile tool. In trace gases analysis, the PA technique provides highly sensitive and selective detection, enabling measurements of various trace gases with applications ranging from environmental monitoring to industrial safety. In solid-state analysis, PA offers valuable insights into mechanical properties, structural characteristics, and composition, supporting non-destructive testing with high precision. Moreover, PA has revolutionized medical diagnostics, facilitating early cancer detection and cardiovascular monitoring. However, some challenges in PA applications include the selection of a suitable experimental setup, calibration, high-power laser control, the complexity of PA signal generation, and solving the inverse problem. Since ML continues to develop as a robust, efficient, and precise tool, its role in optimizing PA technique is likely to expand. The main challenge in the future can be the practical implementation of ML software tailored by PA experimental setup.

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