High Sensitivity Continuous Monitoring of Chloroform Gas by Using Wavelength Modulation Photoacoustic Spectroscopy in the Near-Infrared Range

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Abstract: An optical system for gaseous chloroform (CHCl₃) detection based on wavelength modulation photoacoustic spectroscopy (WMPAS) is proposed for the first time by using a distributed feedback (DFB) laser with a center wavelength of 1683 nm where chloroform has strong and complex absorption peaks. The WMPAS sensor developed possesses the advantages of having a simple structure, high-sensitivity, and direct measurement. A resonant cavity made of stainless steel with a resonant frequency of 6390 Hz was utilized, and eight microphones were located at the middle of the resonator at uniform intervals to collect the sound signal. All of the devices were integrated into an instrument box for practical applications. The performance of the WMPAS sensor was experimentally demonstrated with the measurement of different concentrations of chloroform from 63 to 625 ppm. A linear coefficient \( R^2 \) of 0.999 and a detection sensitivity of 0.28 ppm with a time period of 20 s were achieved at room temperature (around 20°C) and atmosphere pressure. Long-time continuous monitoring for a fixed concentration of chloroform gas was carried out to demonstrate the excellent stability of the system. The performance of the system shows great practical value for the detection of chloroform gas in industrial applications.

Keywords: wavelength modulation; photoacoustic; chloroform gas; DFB laser; high sensitivity

1. Introduction

Chloroform, as a member of the group referred to as volatile organic compounds (VOCs), appears widely in industrial activities. It is commonly used as reagent, anesthetic, refrigerant, and organic solvent [1]. Chloroform has moderate toxicity and a strong volatile nature. Inhalation of chloroform vapor can paralyze the nervous system. When in an environment of 900 ppm chloroform, people may become dizzy in a very short time [2]. In addition, chloroform is unstable when exposed to light in the air. It will react with the oxygen and gradually decomposes to produce highly toxic phosgene and hydrogen chloride. Therefore, the development of gaseous chloroform monitoring system has significant importance and has drawn much attention.

After a long period of development, optical methods have matured and are commonly used in substance detection. Compared with electrochemical and other traditional methods, optical methods possess the advantages of good selectivity, fast response, and high accuracy. In the field of gas sensing, absorption spectroscopy technology has been developed rapidly. In recent years, differential optical absorption spectroscopy (DOAS) [3–5] plays an important role in gas detection and is mainly used in the ultraviolet band. Cavity-enhanced absorption spectroscopy (CEAS) [6–9] and cavity ring-down absorption spectroscopy (CRAS) [10,11] are the other two most commonly employed optical methods. In these
systems, high reflection mirrors (>99.99%) are used as the window of the gas cell, and consequently the maintenance of the mirrors has always been an important issue. Non-dispersive infrared (NDIR) [12,13] and tunable diode laser absorption spectroscopy (TDLAS) [14–18] have also been well developed for optical gas detection over these years. Despite the relatively low stability, more and more products have been developed based on NDIR because of its low cost and fast response. With the rapid development of tunable lasers, great progress in the TDLAS technology has also been achieved, although its measurement sensitivity is largely limited by the optical length.

Photoacoustic spectroscopy (PAS), as a well-established optical method, is widely used for trace gas analysis due to its simplicity and wide dynamic range [19]. The principle of the photoacoustic (PA) effect has been discussed for more than a century [20]. Recently, quartz-enhanced photoacoustic spectroscopy (QEPAS) with high sensitivity has been demonstrated in detail [21]. QEPAS relies on the resonant effect of a small quartz tuning fork to greatly enhance the PA signal with a high quality factor around 10,000 [22]. However, in most cases, QEPAS has a strict requirement on the beam quality of light spots and the quartz fork that needs to be replaced regularly, which undoubtedly increases the complexity of the system. Traditional PA sensors using electret microphones effectively overcome these issues, as the PA effect depends on an acoustic resonant cavity with typical resonator diameters of 4–10 mm [23,24], larger than the conventional laser spot. The simple structure of the acoustic resonator leads to the broad applications of gas detection function in environmental monitoring, atmospheric research, and industrial process control [25].

In some conditions, a mechanical chopper was used to modulate light intensity due to the difficulty of light source modulation, such as in a radiation source [26]. Electrical modulation in tunable light sources can get rid of the mechanical chopper to simplify the system structure. In 2005, S. Civiš et al. used diode lasers (DL) to detect the NH$_3$, and got a detection limit of 1 ppm [27]. For further improvement of the detection sensitivity, wavelength modulation spectroscopy (WMS) technology is coupled to PAS to eliminate the background noise. As an example, in 2016, Wang et al. utilized WMPAS to achieve the detection of NH$_3$, CO$_2$, and H$_2$O, and got minimum detection limits of 6 ppb, 5 ppm, and 29 ppm, respectively [28]. In 2018, Wang et al. theoretically explained the principle of WMPAS technology and experimentally demonstrated it through the detection of water vapor [29]. WMPAS is suitable for use in the gas sensing area due to its advantages of good selectivity, high-sensitivity, and no-destructiveness.

In this paper, we elaborated a WMPAS system for gaseous chloroform detection for the first time in the near infrared range by utilizing a DFB laser emitting at 1683 nm with a light power of 24.5 mW. A home-made PA resonator with a resonance frequency of 6390 Hz was employed, and a multi-microphones approach was used to improve the PA signal. To make the system compact, we used the data acquisition (DAQ) card to generate analog signals for modulation, and replaced the huge desk type lock-in amplifier with a board-type one. Finally, all of the devices were integrated into a 39 cm \times 40 cm \times 20 cm chassis for convenience and practical use. In view of the complex absorption spectrum of chloroform in this spectral range, our laser scanning spectrum covered its two adjacent absorption peaks to observe and analyze the influence. Different concentrations of chloroform gas were measured at the room temperature and atmosphere pressure, and the results show the excellent performance of the system, which indicates great practical value for chloroform gas detection.

2. Materials and Methods

2.1. Principle

Wavelength modulation photoacoustic spectroscopy technology has been discussed in detail by previous works [29–33]. In the WMPAS system, the lock-in amplifier is a key element for demodulating PA signal at the resonance frequency [34]. The first harmonic signal derived from the PA signal can be simply given by [29]:

$$S_{1f} = S_m CF I_0 \times H_1(\nu) \cos(\varphi)$$

(1)
where \( S_m \) represents the microphone sensitivity, \( F \) is the response constant of PAS cell, \( C \) stands for the gas concentration, \( I_0 \) denotes the light intensity, \( H_1(\nu) \) is the first harmonic magnitude derived from the Fourier cosine series expansion of the gas absorption, and \( \varphi \) is the phase difference between the detected PA signal and the reference signal.

Apparently, the harmonic signal is affected by the phase difference of the detection and reference signals. To get the in-phase output signal, it is necessary to adjust the phase of the reference signal to match the phase of PA signal in real-time. The phase influence can be solved by generating two orthogonal components, \( X_{nf} \) and \( Y_{nf} \), at the lock-in output and then calculate the \( nf \) magnitude by making the root square of them. Taking the 1f signal as an example, the formula can be expressed as [30]:

\[
R_{1f} = \sqrt{X_{1f}^2 + Y_{1f}^2}
\]  

where \( X_{1f} \) and \( Y_{1f} \) denote the demodulated signals acquired by using two orthogonal reference signals, a cosine one and a sine one, with the same frequency of the modulation signal, respectively.

In this way, the phase shift is avoided while the 1f signal value remains positive all the time. Therefore, in contrast to the common 1f signal that has a valley and a peak, it has two positive peaks.

2.2. System Setup

The experiment schematic diagram of PAS is depicted in Figure 1. A near-infrared DFB (Distribute Feedback, NEL, Tokyo, Japan) laser with a center wavelength of 1683 nm and a light power of 24.5 mW was selected as the light source. A laser driver (ITC102, Thorlabs, Newton, USA) was employed to precisely control the current and temperature of the laser to cover the absorption line of CHCl\(_3\) at 1683 nm. An analog modulation signal combined with a high-frequency sine wave and a low-frequency sawtooth wave was generated by a DAQ card (USB-6211, National instrument, Austin, TX, USA) and imposed on the laser driver. The space light emitted from the pigtail of the laser was collimated by a collimator (F280APC-1550, Thorlabs, Newton, USA) and the beam was converged in the center of the PA cell through a quartz lens (\( f = 100 \) mm) coated with near infrared anti-reflective coating. To reduce the intensity loss of the laser, the windows of the PA cell were made of CaF\(_2\) with a strong transmittance (>90%) in the near-infrared band. The resonant cavity of the PA cell made by stainless steel has a resonate frequency around 6390 Hz, as shown in Figure 2. Different from the quartz tuning fork, the resonant cavity has a wide frequency response range. The resonant cavity we used had a slight response difference around 6390 Hz.

Around the middle part of the resonant cavity, eight microphones (FG-23329-P07, Knowles, Itasca, USA) were evenly distributed to receive the sound signals produced by the chloroform gas during the measurement. A pair of Mass Flow Controllers (MFCs) with a maximum flow rate of 1 L/min and an error of 1 mL/min were used to mix the chloroform gas with the pure nitrogen. The buffer zones on the edge of two sides were used to reduce the sound interference caused by the gas flow. The PA signal was processed through a home-made preamplifier which possesses a high pass filter and a function of signal amplification at the same time. A dual-phase lock-in amplifier (LIA-BVD-150-L, Femto, Berlin, Germany) with a sinusoidal reference signal given by the DAQ card was used for further demodulation. Finally, the signal was transmitted to the laptop for display through a program written using the LabVIEW software.
2.3. Absorption Lines and Laser Performance

Figure 3a presents the absorption cross-section of chloroform near 1683 nm with five absorption peaks ranging from 1682 nm to 1684 nm according to the HITRAN database [35]. The intensity of the absorption peak increased as the wavelength increased. The maximum intensity of the absorption peak almost achieved the order of $10^{-19}$ cm$^2$/molecule at 1683.15 nm, which was used as target peak for measuring chloroform to get the best PA signal. Furthermore, to observe the influence imposed on the PA signal by the adjacent absorption peak, we scanned the injected current of the laser in a large scale, leading to a wide wavelength scanning range, so as to completely cover the target and the adjacent absorption peak.

The performances of the DFB laser used measured by an optical spectrum analyzer (AQ6317, ANDO Electric, Tokyo, Japan) and an optical power meter (PM100D, Thorlabs, Newton, MA, USA) were plotted in Figure 3b. As the injected current increased from 30 mA to 150 mA with a step length of 10 mA, the emission wavelength of the laser was gradually enlarged from 1682.74 nm to 1683.48 nm while the output power of the laser changed from 3.3 mW to 24.5 mW. Unlike common DFB lasers, its wavelength is not linearly tuned and the wavelength change accelerated with the increase of the injection current. During the experiment, we fixed the laser temperature at 19.8 °C and set the initial current at 84 mA.
to get an emitting wavelength of 1682.99 nm. A low-frequency sawtooth wave with an amplitude ranging from $-1.25$ V to $1.25$ V, together with a high-frequency sine wave whose amplitude ranged from $-240$ mV to $240$ mV, were imposed on the laser driver. The driver had a response coefficient of $40$ mA/V, so the sawtooth wave led to a 100-mA change in the injected current that derived the wavelength varying from 1682.76 nm to 1683.34 nm, while the sine wave brought a 19.2-mA current change.

Figure 3. Wavelength-dependent absorption cross-section of gaseous chloroform and wavelength-tuning together with output power of the laser. (a) The absorption cross-section value of the chloroform gas around 1683 nm; the colored area was scanned by the laser. (b) The laser wavelength and the output power tuned by the injected current at the experiment temperature of 19.8 °C.

3. Results

3.1. Calibration

Wavelength modulation spectroscopy (WMS) is one of the most effective techniques for eliminating the background noise for PAS measurement. To get the first harmonic (1f) signal, the resonant frequency of the resonator ($f = 6390$ Hz) determined the frequency of the sinusoidal modulation signal, which was simultaneously sent to the laser driver and the lock-in amplifier. An $R$ value of the 1f PA signal, demodulated from the lock-in amplifier with an integrated time of 1 s, was acquired by the DAQ card (USB-6211, National instrument, Austin, TX, USA). Meanwhile, a sawtooth wave with the frequency of 50 mHz, representing a period of 20 s, was applied to slowly change the laser wavelength. The USB-6211 DAQ card has a maximum single channel sample rate of 250 kS/s. In the experiment, since all of the modulation signals were generated by the DAQ card, a high sample rate was required to ensure the signals would not be distorted. In addition, due to the relatively long sampling time, the sample rate should be limited in a certain range to avoid excessive sample points. Finally, the sample rate of 50 kS/s was set, which resulted in acquiring one million data points in one scanning period. We diluted the chloroform by mixing it with pure nitrogen through the MFCs. Different concentrations ranging from 63 to 625 ppm were generated by adjusting the flow rate of the two gas paths. In order to reduce the influence of airflow, the total flow rate was controlled to remain below 0.4 L/min. The 1f PA signals of different chloroform concentrations were integrated into one graph, as shown in Figure 4. The signal of pure nitrogen was regarded as the base signal.
As can be seen in Figure 3b, the wavelength shows a poor linear relationship with the injected current. During the experiment, the current increased linearly with time, which resulted in a nonlinear change of the wavelength. The wavelengths at corresponding time were given on the top X-axis. Obviously, four different peaks emerged in Figure 4, belonging to the 1f PA signal of the two adjacent absorption peaks of chloroform, separately. This indicates that the two absorption peaks of chloroform can clearly be distinguished, which reflects the capability of WMPAS in dealing with unconventional absorption lines. Generally, the intensity of the 1f signal was approximately proportional to the first derivative value of the gas absorption cross-section [17]. Due to the influence of adjacent absorption lines, the gas absorption cross-section was no longer the conventional Voigt type which is usually used to describe the broadening of the gas absorption line under normal pressure, and the amplitude of the 1f PA signal was affected accordingly.

The intensity of the last peak (colored area) in Figure 4 was selected to retrieve chloroform concentration, as the peak amplitudes free-interference from other gas species (as discussed in Section 3.4) and the absorption shape at this frequency is close to the normal first harmonic curve. When the concentration of chloroform was 625 ppm, the peak value of the signal reached 3.75 mV, and the peak value decreased proportionally with the decrease in the gas concentration. Although improving the amplitude of the sine wave can enlarge the value of the peak signal, it will also broaden the 1f PA signal [33]. The large amplitude of the low-frequency sawtooth scanning wave led to an injected current variation range of 100 mA, while the maximum current modulation range of the laser was about 150 mA, which limited the amplitude range of the high-frequency sine wave.

For the ten different concentrations of chloroform gas, magnitude measurements were carried out and the results were well sorted and analyzed. Each concentration was measured three times and the standard deviation of the results was calculated as the measurement error. The relationship between the 1f PA signal intensity and gas concentration was shown in Figure 5 with good linear relationship between the signal intensity and gas concentration \(y = 0.059x + 0.03\), and the square of the coefficient \(R\) of 0.999.
Figure 5. Relationship between the chloroform concentration and the measured signal intensity. Ten different concentrations of chloroform gas were measured in the experiment.

3.2. Continuous Measurement of Different Concentrations

In practical applications, continuous monitoring capability and response ability are two important indexes to evaluate the system. In the experiment, the calibration curve determined by the data in Figure 5 was used to retrieve the known concentrations of chloroform gas. The flow rates of the two gas paths were controlled by the MFCs. One path was pure nitrogen, while the other path was for chloroform. By changing the flow rate of the two paths, we gradually increased the concentration of chloroform gas inside the PA cell from 104 ppm to 625 ppm (104 ppm, 156 ppm, 208 ppm, 313 ppm, 417 ppm, 469 ppm, 521 ppm, 563 ppm, 625 ppm), while the total airflow velocity was always kept to less than 0.4 L/min to reduce the impact of the airflow sound during the whole process, and the gas was continuously flowing through the PA cell. Figure 6 shows the continuous measurement results for more than half an hour. Apparently, the system has the ability to quickly respond to the change in gas concentration. The numerical instability may be caused by airflow disturbance. The calculation results indicate that compared with the theoretical proportioning concentration, and the measurement error is controlled within ±3% for all concentrations, which demonstrates the high measurement accuracy of the system.

Figure 6. Continuous measurement of the chloroform gas with the concentration gradually increasing from 104 ppm to 625 ppm. The process lasted for over 40 min.
3.3. Allan Variance

The stability of the instrument system is of vital importance. To test the stability of the system, we implemented continuous measurement for a fixed concentration of chloroform gas for 4000 s. During this experiment, 104 ppm chloroform gas was obtained through setting the flow rates of the pure nitrogen path and 625 ppm chloroform path at a ratio of 5:1. The target gas was continuously flowing through the PA cell at a total flow rate of 0.3 L/min, and the PA cell was always kept at room temperature (about 20 °C) and atmospheric pressure. The system got a data point of chloroform gas concentration every 20 s, so a total of 200 data points were obtained in 4000 s. As shown in the upper left corner of Figure 7, the collected concentration data fluctuated around 104 ppm (from 102 ppm to 105 ppm), and the measurement error was limited within ± 2%. Allan-Werle variance analysis is widely used to evaluate the sensitivity of a gas detection system. By calculating the Allan-Werle variance of the measured data, we found the theoretical detection sensitivity under different averaging times. We achieved a sensitivity of 0.28 ppm with a time period of 20 s (no averaging) and a sensitivity of 10 ppb with an averaging time of 500 s, respectively. This means that our system has the ability to accurately detect low concentrations of chloroform gas.

![Graph showing Allan-Werle deviation analysis](image)

**Figure 7.** Plot of continuously measured data (at every 20 s) of chloroform gas concentration over 1 h and the corresponding Allan-Werle deviation analysis as the measurement time length (for averaging over each period of 20 s) increases.

3.4. Anti-Interference

Dichloromethane (CH₂Cl₂) and chloroform have similar properties and are both commonly used as solvents in some industries, therefore, dichloromethane and chloroform often exist at the same time in industrial environments. In this case, when the system is used for chloroform gas detection, it must remove the interference of dichloromethane gas. Although there is no obvious absorption peak of dichloromethane in this band, it is necessary to experimentally determine the interference from high concentrations of dichloromethane. In this work, dichloromethane gas with a concentration of 1052 ppm was used to verify the interference. Figure 8 shows the acquired 1f PA signals of pure nitrogen (black line), 1052 ppm dichloromethane (red line), 526 ppm dichloromethane with 313 ppm chloroform (blue line), and 313 ppm chloroform alone (green line), respectively. Obviously, in the effective area (colored area), 526 ppm Dichloromethane, and nitrogen have the same effect on the detection of chloroform, which is shown by the consistency of peak values between the blue line and the green line. This demonstrates that, in this area, even a high concentration of dichloromethane (e.g., up to 526 ppm) will not have any impact on the detection of chloroform gas.

![Graph showing PA signals of different gases](image)
Figure 8. Interference experiment of dichloromethane on chloroform. If PA signals of different kinds of gases are plotted with a scanning period of 20 s (colored area is the selected effective area).

4. Conclusions

In this work a compact WMPAS system for continuous gaseous chloroform monitoring using a home-made PA cell combined with eight microphones has been first demonstrated in detail. The application of WMPAS technology with a high-power DFB laser makes it possible to measure chloroform with high sensitivity in near infrared, and a detection sensitivity of 0.28 ppm with a time period of 20 s was achieved at room temperature (around 20 °C) and atmospheric pressure. To observe the influence of the adjacent absorption peak, we increased the laser wavelength covering range to 0.58 nm, which limited the modulation depth and sacrificed part of the signal intensity at the same time. The results indicate that WMPAS possesses excellent capability in the detection of gas with complex absorption cross-section.

Different concentrations of chloroform gas were measured in sequence and the results have shown a good linear relationship between the 1f PA signal intensity and the gas concentrations. A $R^2$-square value of 0.999 was achieved when the gas concentration was less than 625 ppm, which proves the reliability of the system. Long-term monitoring was carried out to evaluate the stability of the system, and the measurement error was limited within ±2%, which adequately illustrates the good stability performance of the system. A series of comparative experiments were also been carried out to prove the good anti-interference of dichloromethane on the detection of chloroform. The overall performance of the system has shown great promise for chloroform gas monitoring in industrial applications. In addition, the performance can be greatly improved if combines the system with multi-pass scheme [36].

Author Contributions: T.Z. and G.W. designed/modified the experimental setup, T.Z. performed the experiments and analyzed the data. T.Z. wrote the software. T.Z. wrote the manuscript. S.H. and Y.X. supervised the work and finalized the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Key Research and Development Program of Zhejiang Province (grant number 2021C03178), NingboTech University (grant number 1141257B20200538), Zhejiang University NGICS Platform, and National Natural Science Foundation of China (11621101).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.
Data Availability Statement: Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

Acknowledgments: The authors are grateful to Yiming Jiang, and Lihui Wang for valuable discussion and help.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Stroo, F.; Hans, W. In Situ Remediation of Chlorinated Solvent Plumes; Springer: New York, NY, USA, 2010; pp. 4–14.
2. Mohebbifar, M.R. High-sensitivity detection and quantification of CHCl 3 vapors in various gas environments based on the photoacoustic spectroscopy. Micros. Opt. Technol. Lett. 2019, 61, 2234–2241. [CrossRef]
3. Cao, X.-H.; Li, J.; Gao, H.; Du, Z.-H.; Ma, Y.-W. Simultaneous Determination of Carbon Disulfide, Carbon Monoxide, and Dinitrogen Oxide by Differential Absorption Spectroscopy Using a Distributed Feedback Quantum Cascade Laser. Anal. Lett. 2017, 50, 2342–2350. [CrossRef]
4. Yu, S.; Yan, L.; Zhang, T.; Zhang, Y.; Zhang, X.; Sun, G.; William, W.Y. Gas detection based on quantum dot LEDs utilizing differential optical absorption spectroscopy. Micros. Opt. Technol. Lett. 2017, 7, 30996–30100. [CrossRef]
5. Al-Jalal, A.; Al-Basheer, W.; Gasmi, K.; Romadhon, M.S. Measurement of low concentrations of NO2 gas by differential optical absorption spectroscopy method. Measurement 2019, 146, 613–617. [CrossRef]
6. Wang, P.; Chen, W.; Wan, F.; Wang, J.; Hu, J. A review of cavity-enhanced Raman spectroscopy as a gas sensing method. Appl. Spectrosc. Rev. 2019, 55, 393–417. [CrossRef]
7. Zheng, K.Y.; Zheng, C.T.; Zhang, Y.; Wang, Y.D.; Tittel, F.K. Review of Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy (IBBCEAS) for Gas Sensing. Sensors 2018, 18, 3646. [CrossRef] [PubMed]
8. Amiot, C.; Aalto, A.; Ryczkowski, P.; Toivonen, J.; Genty, G. Cavity enhanced absorption spectroscopy in the mid-infrared using a supercontinuum source. Appl. Phys. Lett. 2017, 111, 061103. [CrossRef]
9. Chandran, S.; Mahon, S.; Ruth, A.A.; Bradlell, J.; Gutiérrez, M.D. Cavity-enhanced absorption detection of H2S in the near-infrared using a gain-switched frequency comb laser. Appl. Phys. A 2018, 124, 1–9. [CrossRef]
10. Maity, A.; Maithani, S.; Pradhan, M. Cavity Ring-Down Spectroscopy: Recent Technological Advancements, Techniques, and Applications. Anal. Chem. 2021, 93, 388–416. [CrossRef]
11. Liu, A.W.; Hu, C.L.; Wang, J.; Perevalov, V.I.; Hu, S.M. Cavity ring-down spectroscopy of 15N enriched N2O near 1.56 µm. J. Quant. Spectrosc. Radiat. Transf. 2019, 232, 1–9. [CrossRef]
12. Wang, H.Y.; Wang, J.; Ma, X.Y.; Chen, W.L.; Chen, D.; Li, Q.F. Note: A NDIR instrument for multicomponent gas detection using the galvanometer modulation. Rev. Sci. Instrum. 2017, 88, 116103. [CrossRef] [PubMed]
13. Tan, X.; Zhang, H.; Li, J.; Wan, H.; Guo, Q.; Zhu, H.; Liu, H.; Yi, F. Non-dispersive infrared multi-gas sensing via nanoantenna integrated narrowband detectors. Nat. Commun. 2020, 11, 1–9. [CrossRef] [PubMed]
14. Lou, X.; Somesfalean, G.; Svanberg, S.; Zhang, Z.; Wu, S. Detection of elemental mercury by multimode diode laser correlation spectroscopy. Opt. Express 2012, 20, 4927–4938. [CrossRef]
15. Lin, H.; Lou, X.; Zhong, W.; He, S. Continuous monitoring of elemental mercury employing low-cost multimode diode lasers. Mass. Sci. Technol. 2015, 26, 085501. [CrossRef]
16. Lou, X.; Zhang, T.; Lin, H.; Gao, S.; Xu, L.; Wang, J.; Wan, L.; He, S. Detection of gaseous mercury using a frequency-doubled green diode laser. Opt. Express 2016, 24, 27509–27520. [CrossRef]
17. Lin, H.; Gao, F.; Ding, Y.; Yan, C.; He, S. Methane detection using scattering material as the gas cell. Appl. Opt. 2016, 55, 8030. [CrossRef]
18. Zhang, T.; Lou, X.; Xu, L.; He, S. Elemental mercury sensing by synchronously sweeping two multimode diode lasers. Appl. Opt. 2020, 59, 3360–3368. [CrossRef] [PubMed]
19. Besson, J.-P.; Schilt, S.; Thévenaz, L. Multi-gas sensing based on photoacoustic spectroscopy using tunable laser diodes. Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 2004, 60, 3449–3456. [CrossRef]
20. Bell, A.G. On the production and reproduction of sound by light. Am. J. Sci. 1880, 20, 305–324. [CrossRef]
21. Kosterov, A.A.; Bakhirkin, Y.A.; Curl, R.F.; Tittel, F.K. Quartz-enhanced photoacoustic spectroscopy. Opt. Lett. 2002, 27, 1902–1904. [CrossRef]
22. Ma, Y. Review of Recent Advances in QEPAS-Based Trace Gas Sensing. Appl. Sci. 2018, 8, 1822. [CrossRef]
23. Elia, A.; Di Franco, C.; Lugara, P.M.; Scammarco, G. Photoacoustic Spectroscopy with Quantum Cascade Lasers for Trace Gas Detection. Sensors 2006, 6, 1411–1419. [CrossRef]
24. Dumitras, D.C.; Dutu, D.C.; Matei, C.; Magureanu, A.M.; Petrus, M. Laser photoacoustic spectroscopy: Principles, instrumentation, and characterization. J. Optoelectron. Adv. Mater. 2007, 9, 3655–3701.
25. Choi, H.; Ryu, J.-M.; Choe, S.-W. A novel therapeutic instrument using an ultrasound-light-emitting diode with an adjustable telephoto lens for suppression of tumor cell proliferation. Measurement 2019, 147, 106865. [CrossRef]
26. Wang, G.; Kulinski, P.; Hubert, P.; Deguine, A.; Petitprez, D.; Crumeyrolle, S.; Fertein, E.; Deboudt, K.; Flament, P.; Sigrist, M.W.; et al. Filter-free light absorption measurement of volcanic ashes and ambient particulate matter using multi-wavelength photoacoustic spectroscopy. Prog. Electromagn. Res. 2019, 166, 59–74. [CrossRef]
27. Civiš, S.; Horká, V.; Cihelka, J.; Šimeček, T.; Hulicius, E.; Oswald, J.; Pangrác, J.; Vicet, A.; Rouillard, Y.; Salhi, A.; et al. Room-temperature diode laser photoacoustic spectroscopy near 2.3 μm. *Appl. Phys. B* **2005**, *81*, 857–861. [CrossRef]

28. Wang, J.; Wang, H. Ammonia, carbon dioxide and water vapor detection based on tunable fiber laser photoacoustic spectroscopy. *Opt.* **2016**, *127*, 942–945. [CrossRef]

29. Wang, Z.L.; Tian, C.W.; Liu, Q.; Chang, J.; Zhang, Q.; Zhu, C.G. Wavelength modulation technique-based photoacoustic spectroscopy for multipoint gas sensing. *Appl. Opt.* **2018**, *57*, 2909–2914. [CrossRef]

30. Salati, S.H.; Khorsandi, A. Apodized 2f/1f wavelength modulation spectroscopy method for calibration-free trace detection of carbon monoxide in the near-infrared region: Theory and experiment. *Appl. Phys. A* **2013**, *116*, 521–531. [CrossRef]

31. Choi, S.S.; Mandelis, A.; Guo, X.; Lashkari, B.; Kellnberger, S.; Ntziachristos, V. Wavelength-Modulated Differential Photoacoustic Spectroscopy (WM-DPAS) for noninvasive early cancer detection and tissue hypoxia monitoring. *J. Biophotonics* **2016**, *9*, 388–395. [CrossRef]

32. Schilt, S.; Thévenaz, L. Wavelength modulation photoacoustic spectroscopy: Theoretical description and experimental results. *Infrared Phys. Technol.* **2006**, *48*, 154–162. [CrossRef]

33. Chen, K.; Liu, S.; Mei, L.; Jin, F.; Zhang, B.; Ma, F.; Chen, Y.; Deng, H.; Guo, M.; Yu, Q. An auto-correction laser photoacoustic spectrometer based on 2f/1f wavelength modulation spectroscopy. *Analyst* **2020**, *145*, 1524–1530. [CrossRef] [PubMed]

34. Wang, Q.; Wang, Z.; Ren, W. Wavelength-stabilization-based photoacoustic spectroscopy for methane detection. *Meas. Sci. Technol.* **2017**, *28*, 065102. [CrossRef]

35. Gordon, I.E.; Rothman, L.S.; Hill, C.; Kochanov, R.V.; Tan, Y.; Bernath, P.F.; Birk, M.; Boudon, V.; Campargue, A.; Chance, K.V.; et al. The HITRAN2016 molecular spectroscopic database. *J. Quant. Spectrosc. Radiat. Transf.* **2017**, *203*, 3–69. [CrossRef]

36. Qiao, S.; Ma, Y.; Patimisco, P.; Sampaolo, A.; He, Y.; Lang, Z.; Tittel, F.K.; Spagnolo, V. Multi-pass quartz-enhanced photoacoustic spectroscopy based trace gas sensing. *Opt. Lett.* **2021**, *46*, 977–980. [CrossRef]