Photoacoustic Spectroscopy in Trace Gas Monitoring

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Gas-phase spectroscopy is nowadays very common in a wide variety of fields next to chemistry and physics, ranging from atmospheric chemistry to biology, medical sciences, and safety. Spectroscopic gas sensors have proven to be indispensable tools for these areas. There are various ways of utilizing gas sensors, and each application puts different demands. Some applications require a very high sensitivity for one specific gas compound, while others benefit more from a sensor that has the ability to measure a wide range of gases or benefit from a miniaturized footprint. A high time resolution is also desirable, as well as selectivity, robustness, and little or no need for sample preparation and maintenance; photoacoustic spectroscopy and their sensors meet a large number of these demands. This article discusses photoacoustic spectroscopy as sensitive, real-time, and noninvasive tool for trace gas monitoring. After an introduction and historic overview, attention is focused onto the description of devices and equipment; they determine the detection limits and selectivity. Applications are discussed with emphasis on atmospheric applications, safety, and biological/agricultural applications followed by human health examples. Finally, a comparison is made with other spectroscopy methods.

1 INTRODUCTION

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 gives rise to a temperature increase of the gas, owing 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 to $10^{-2}$ s at 10 μm. For nonradiative decay, these values depend on the pressure (decay time $\tau$ inversely proportional to the pressure) and can vary strongly at atmospheric pressures ($10^{-3}$ to $10^{-8}$ s).

By modulating the radiation 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. Laser-based photoacoustic detectors are able to monitor trace gas concentrations at atmospheric conditions with orders of magnitude better sensitivity per centimeter absorption path length, as compared to conventional scientific instrumentation (see Section 5). In addition, they are able to monitor noninvasively and on-line under dynamic changing conditions.

2 HISTORICAL OVERVIEW

The photoacoustic effect was first reported by Alexander Graham Bell in 1880; he discovered that: ‘… thin discs emitted sound when exposed to a rapidly interrupted beam of sunlight…’. In a later experiment he removed the eyepiece of a commercial spectroscope and placed absorbing substances at the focal point of the
Figure 1 (a) The eyepiece of a spectroscope is removed and substances are placed in the focal point of the instrument behind a slit. These substances are put in contact with the ear by means of a hearing tube. (b) Sunlight is modulated with chopper B and focused onto a glass bulb A.

3 DEVICES AND EQUIPMENT

3.1 Nonlaser Light Sources

Lasers are not essential to operate photoacoustic gas detection systems. Although the spectral power density of broadband infrared lamps is orders of magnitude lower as compared to lasers, they have substantial advantages such as wide wavelength coverage, reliability, and cost-effectiveness. Such infrared lamp sources, in combination with various photoacoustic detection schemes, are commercially available for trace gas detection at parts-per-million-volume (ppmv) levels for a wide range of molecular gases, such as CO, CO₂, NO, N₂O, SO₂, CH₄, C₂H₄, and C₃H₈. Such design is a direct result of the developments made by Luft et al. in the 1950s and 1960s.

In 1938, Viererov refined the photoacoustic method for the first spectroscopic gas analysis; thereafter, Pfund and Luft measured trace gas absorption spectra, with an infrared broadband light source down to the parts-per-million level. After the invention of the laser, at the end of the 1960s, the scientific interest expanded again. In 1968, Kerr and Atwood utilized laser photoacoustic detection to obtain the absorption spectrum of small gaseous molecules. Owing to the high spectral brightness of lasers and improved phase-sensitive lock-in techniques to amplify the acoustic signal, they were able to determine low concentrations of air pollutants. Kreuzer demonstrated that it was possible to detect concentrations of 10 parts per billion volume (1 ppbv = 1·10⁹ mol/mol) of methane in nitrogen, using an intensity-modulated infrared (3 μm) He–Ne laser. Patel et al. demonstrated the application potential by measuring the NO and H₂O concentrations at an altitude of 28 km with a balloon-borne spin-flip Raman laser. From there on, the photoacoustic effect was introduced into the field of spectroscopy with all its environmental, biological, and medical applications.
Figure 2 Infrared gas analyzer with photoacoustic detection scheme to detect a specific gas out of a multicomponent gas mixture, thereby avoiding cross interference (ABB GmbH, Frankfurt). Light from the infrared source is split into two paths. The chopper modulates the intensity for both paths. A filter volume in each path serves to filter out light of wavelengths not needed for the detection process; they can be filled with gases of which the absorption spectra do not overlap with those of the species under scrutiny. M1 and M2 serve as measuring cell and reference cell, respectively. With the help of the equalizer both light intensities become equal before entering the last cell. The last cell consists of two compartments with a membrane in between. Both compartments are filled with the gas under investigation so that all wavelength characteristics for this gas contribute to the signal. If the attenuation differs in M1 from that in M2 the membrane starts to oscillate with the frequency of the chopper. This oscillation (typically a few hertz) is detected capacitively.

Figure 3 Light from an infrared light source is reflected off a mirror and is passed through a mechanical chopper and then through one of the optical filters in the filter wheel (LumaSense Technologies, Denmark). The gas being monitored, causing the temperature of the gas to increase selectively, absorbs the light transmitted by the optical filter. The filter wheel turns so that light is transmitted through the next optical filter, and the new signal is measured. The number of times this step is repeated is dependent on the number of gases being measured. The response time is 30 s if five gases and water vapor are measured.

Simultaneously active. When other gases absorb in the same spectral region, additional absorptions at other wavelengths than the gas of interest will not contribute to the acoustic signal; the light passes the detection cell unattenuated. When a specific compound, e.g., H₂O, causes strong spectral overlap, an extra cell can be placed in the light path filled with the interfering gas. This cell attenuates completely the wavelengths where this interfering molecule absorbs, including the spectral overlap regions. Thus, these wavelengths cannot contribute to the photoacoustic signal, and a single component can be detected out of complex multicomponent gas mixtures.

Spectral selectivity can also be achieved through the use of optical filters, see Figure 3. By installing a number of optical filters in a rotation cartwheel before the light passes through the photoacoustic gas sampling cell, it selects these specific wavelengths at which the gas of interest has it strongest absorption bands. Such a system can measure mixtures of concentrations in any air sample. Detection limit is gas dependent, but is typically in the sub-ppmv region. Such instruments
require no consumables and very little maintenance and are therefore ideally suited for permanent monitoring tasks (environment and industrial).

Instead of using optical filters, higher spectral resolution can be achieved if photoacoustic detection is also combined with Fourier transformed infrared (FTIR) spectroscopy. FTIR is a widely used method for obtaining infrared spectra of a sample. Infrared radiation is split in a Michelson interferometer where half of the light passes through to a fixed mirror and the other half is reflected toward a moving mirror. The two beams recombine and pass through a photoacoustic gas cell where the sample absorbs light at molecule-specific frequencies. Using photoacoustics, a step-scan interferometer is used. The moving mirror is moved in discrete steps and halted at each retardation position at which the interferogram is sampled. After each point is sampled, a Fourier transformation is performed. Within the FTIR, a short, small volume photoacoustic cell is used making use of a Helmholtz resonance. In such a way, sensitivity of gas-phase FTIR is improved to low-ppmv levels for a wide range of gases.\(^{(13,14)}\)

Nowadays, light-emitting diodes (LEDs) are an intermediate alternative with reduced spectral range, but increased power density as compared to infrared lamps. LEDs are very convenient sources for photoacoustics, since they have small size and low power consumption. The full width at half maximum (FWHM) of the emission spectrum is typically 10–20\% of its peak wavelength, which is sufficient for most single gas measurement. The LED output is easily modulated by current pulsing, with frequencies up to several megahertz; its brightness and on/off contrast do not decline as modulation frequency is increased, as with traditional blackbody emitters. With mid-infrared LEDs, photoacoustic trace gas detection is performed in the 3–7\(\mu m\) wavelength range,\(^{(15)}\) using a cantilever instead of a microphone. Detection at the low-ppmv levels can be achieved for gases such as methane, propane, CO\(_2\), and SO\(_2\), with 1-s sample integration time, see Figure 4. Using UV LEDs at 285\(\text{nm}\) as a light source, ozone could be sensed down to 1 ppbv based on quartz-enhanced photoacoustic spectroscopy.\(^{(17)}\) With the same method, an NO\(_2\) sensor was developed using a blue LED down to a detection limit of 1.3 ppbv.\(^{(18)}\)

### 3.2 Laser Light Sources

High spectral brightness renders continuous wave (cw) laser sources ideally, suitable for photoacoustic trace gas detection. At small absorptions, the photoacoustic signal is proportional to the laser power; from the Beer–Lambert law, one finds:

\[
P = P_0 e^{-\sigma N l} \Rightarrow \Delta P = P_0 - P \approx P_0 \cdot \sigma \cdot N \cdot l \tag{1}
\]

with \(\Delta P\) the difference of laser power before and after the photoacoustic cell, \(\sigma\) the absorption cross-section per molecule (in cm\(^2\)), \(N\) the number of absorbing molecules per cm\(^3\), and \(l\) the absorption path length (in cm). The absorbed energy \((P_0 - P)\) is converted into acoustic energy and recorded by a microphone. As can be seen from this equation, for small absorptions the generated acoustical signal is proportional to the incoming laser power (high laser powers are advantageous) and the gas concentration (linearity of the signal). A nonlinear absorption response can occur in specific cases, such as using focused, high-power laser beams. In that case pumping rate by the laser light to a higher rovibrational level exceeds the collisional de-excitation rates, and saturation occurs. Another nonlinear response is caused by kinetic cooling in the gas; the latter is explained later.

At present, photoacoustic detection goes together with bright laser light sources, ranging from the infrared to the visible and UV. The high-power, cw molecular CO and CO\(_2\) lasers were the first lasers to detect trace gases photoacoustically, with high sensitivity and selectivity.\(^{(19)}\)
Both the lasers were for a long time the most used lasers for infrared photoacoustic spectroscopy.\(^{(20–24)}\) Although these lasers have a wide wavelength coverage and high power, owing to their dependence on molecular emission lines, they do not have a full wavelength coverage. The developments in solid-state physics and nonlinear optics have expanded the potential for photoacoustic spectroscopy to other wavelength regions. The recent availability of high-power (cw and pulsed) quantum cascade lasers (QCLs), operating at room temperature with power levels up to 1 W, has boosted photoacoustic spectroscopy in the mid-infrared wavelength region. Commercially available external cavity QCLs, operating single-mode tuning ranges, approach a 300-cm\(^{-1}\) wavelength coverage; QCLs and the related interband cascade lasers (ICLs) operate in the mid-infrared wavelength region from 3 to 24 \(\mu\)m.\(^{(25,26)}\)

For the 2.5–5 \(\mu\)m wavelength region, high-power, periodically poled lithium niobate (PPLN) optical parametric oscillators (OPOs) are available. Nowadays, such OPOs are pumped by high-power, near-infrared (fiber-) lasers with excellent spectroscopic properties (narrow linewidth, Gaussian beam profile, and fast wavelength scanning), which the OPO can convert efficiently into the mid-infrared wavelengths, owing to its instantaneous nonlinear effects.\(^{(27)}\) In the near-infrared wavelength region, lasers are used for high-resolution studies of weak overtone absorption spectra of molecular gases.\(^{(28)}\) Overtone spectroscopy profits from sensitive photoacoustic detection, since one deals with high vibrational excitation, where fluorescence-based techniques do not work. Electronic spectroscopy with light sources in the visible or in the ultraviolet does not immediately ask for photoacoustic detection because other techniques provide more powerful means (e.g. laser-induced fluorescence (LIF) or resonance-enhanced multiphoton ionization).

In the ‘telecom’ wavelength region, around 1.5 \(\mu\)m, diode lasers and diode pumped fiber lasers have the advantage of the technical developments, resulting in a small footprint, reliable tunability, low costs, large lifetime, and low maintenance. Diode lasers are not always in favor to be combined with photoacoustic spectroscopy, owing to their low power; however, in combination with fiber amplifiers this disadvantage can be compensated. Larger tuning ranges can be obtained by external cavity set-ups.\(^{(29)}\)

By using pulsed lasers, the wavelength region can be extended and in combination with gated detection the acoustic signal can be isolated from the surrounding acoustical noise and acoustic background signal and detected by a piezo transducer (or microphone). However, in general, pulsed lasers have high intensity, pulse-to-pulse intensity fluctuations, and a varying intensity profile causing nonlinear effects in molecular absorption, thereby reducing detection sensitivity. The highest photoacoustic detection sensitivities have been achieved for modulated cw lasers. If no other arguments prevail, the use of cw lasers is recommended.

### 3.3 Photoacoustic Cells

#### 3.3.1 Nonresonant Cells

To perform trace gas detection, the ideal photoacoustic cell should amplify the generated sound, originating from the molecular gas absorption, meanwhile rejecting acoustic (and electric) noise and in-phase infrared absorption from other materials. Interfering gases should be distinguished by spectroscopic or physical methods. For gas-phase measurements, mainly resonant cells are combined with modulated cw lasers and lock-in amplifiers; pulsed lasers are combined with piezoelectric detectors and boxcars. These selective amplifiers arise from the necessity to lower acoustic and electric noise levels, thus improving the signal-to-noise ratio (SNR).

Other requirements for photoacoustic cells are a low gas consumption or a fast response; for this the active volume of the cell should be small so that no dilution can take place when the trace gas and its carrier gas flow through the photoacoustic cell. If we consider a nonresonant, cylindrical cell, its performance can be expressed as its efficiency to convert absorbed photon energy into acoustic energy, i.e.\( P_{\text{gas}} = F \cdot \Delta P,\) with\( P_{\text{gas}}\) the generated acoustic pressure in the gas and \(\Delta P\) derived from Equation (1). The cell constant \(F\) in \((\text{Pa} \cdot \text{m}^{-1})\) can be derived by:

\[
F_{\text{non resonant}} = \frac{G(\gamma - 1)v_{\text{nr}}}{2\pi \nu V_{\text{nr}}}
\]

with \(l_{\text{nr}}\) and \(V_{\text{nr}}\) the length and the volume of the nonresonant (nr cell), respectively, \(\gamma\) the specific heat constant, \(\nu\) the modulation frequency, and \(G\) a geometrical factor in the order of 1.\(^{(30)}\) From the above formula, one can derive that \(F\) is independent of the cell length. The diameter should be as small as possible to generate high signals, just large enough to allow proper alignment of the incident light beam. To minimize the detection of absorption by the cell windows, one has to maximize the cell length; the energy absorbed by the windows is then distributed over a larger volume. The photoacoustic signal decreases with higher modulation frequencies; therefore, it is advantageous to use low modulation frequencies.

#### 3.3.2 Resonant Cylindrical Cells

In a resonant cell, the modulation frequency is chosen to match one of the resonant frequencies of the cell.
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This produces a standing, amplified sound wave in the resonator. For a gas-type resonant cell, two varieties of acoustical resonators have found widespread use: the Helmholtz resonator and the cylindrical resonator excited in a longitudinal, radial, and/or azimuthal mode (Figure 5).

For cylindrical resonant cells, one has to multiply the cell constant $F$ (Equation 2) with the quality factor $Q$ of the generated acoustic resonance:

$$F_{\text{resonant}} = \frac{G(\gamma - 1)\nu Q}{2\pi V_r}$$  \hspace{1cm} (3)

with $l_r$ and $V_r$ the length and the volume of the acoustic resonator, respectively; $Q$ equals the ratio of the energy stored in the acoustical standing wave over the energy losses per cycle. For resonant cylindrical cells, one can derive for the cell constant:

$$F_{\text{resonant}} \propto \frac{\sqrt{l_r}}{R}$$  \hspace{1cm} (4)

with $R$ the radius of the resonator.\(^{30}\) Cell geometries with large diameter-to-length ratios, to excite the resonance in the radial or azimuthal acoustic mode, possess high $Q$-values and high resonance frequencies. However, they have low $F$-values. Photoacoustic cells with high $Q$-values are sensitive to long-term drifts, owing to temperature fluctuations (speed of sound is temperature dependent). Such cells require active locking of the modulation frequency on the resonance frequency of the cell. Besides, such cells pickup easily acoustical surrounding noise.

In longitudinally excited resonators, a smaller acoustic gain, as a consequence of a relatively low $Q$-value, is compensated for by the signal gain due to the smaller diameter (Equation 4, Figure 6). The resonant acoustical amplification is limited by various dissipation processes, which can be divided into surface and volume effects. The main losses are viscous and thermal losses at the resonator surface, microphone losses, and acoustic wave scattering losses at obstacles inside the cell. The less-important volumetric losses are radiation losses, free-space viscous and thermal losses, and dissipative relaxation processes within the absorbing gases. For a cylindrical resonator, the resonant frequencies are given by\(^ {32}\) (Figure 5):

$$\nu_{k,m,n} = V_s \left\{ \frac{\alpha_{n,m,n} d}{d} \right\}^2 + \left\{ \frac{k}{2\pi} \right\}^{1/2}$$  \hspace{1cm} (5)

with $V_s$ the sound velocity of the gas inside the cavity, $d$ the cell diameter, $l$ the axial length, $k=0,1,2,3,\ldots$ the axial mode numbers, and $\alpha_{n,m,n}$ the $n$th root of the derivative of the Bessel function: $dJ_m/dr = 0$ at $r = R$ (e.g. $\alpha_{0,0} = 0, \alpha_{1,0} = 1.2197, \alpha_{1,1} = 0.5861$, and $\alpha_{1,1} = 1.6970$).

3.3.3 Helmholtz Resonant Cells

Another type of resonant cell is a Helmholtz resonator; it consists of a closed volume (cavity) connected via a long narrow tube to the microphone (Figure 7). It is the acoustic equivalent of a mechanical oscillator composed of a mass (long tube) and a spring (cavity). The oscillation frequency ($\nu_H$) of the system depends on the length ($l_H$), the cross-section ($A_H$) of the tube (or duct), and the volume ($V_H$) of the cavity via the following relation:

$$\nu_H = V_s \left\{ \frac{A_H}{V_H/\nu} \right\}^{1/2}$$  \hspace{1cm} (6)

with $V_s$ the velocity of sound.\(^ {21}\) Although the acoustical response of such a resonator is somewhat lower as compared to cylindrical resonators, it has advantages when low or high temperatures are needed. Microphones have a limited operating temperature. When gases are investigated at low (e.g. 80 K) or high (350 K) temperatures, it is advantageous to have a homogeneous
Figure 6 Two photoacoustic cell types successfully used in trace gas detection. (a) A banana-shaped cell, where the laser beam enters from the left through a Brewster window (BW) to leave the central part \( l = \lambda/2 \) of the resonator at the right Brewster window. The position of the microphone \( M \) is indicated. The two pieces of length \( \lambda/4 \) before and after the bends serve to suppress the window signal, which are at the pressure nodes of the standing acoustic wave. The total length of the banana cell amounts to \( \lambda \). Also, at the bends are the gas inlet and outlet (Gi and Go). (Reproduced with permission from Ref. 31. © Springer-Verlag, 1987.) (b) The open-organ-tube cell; the main part is manufactured of a block of massive material (e.g. brass) to suppress pickup from the surrounding noise. The central part acts as an open acoustical resonator with length \( \lambda/2 \); the resonator tube itself has a highly polished, gold-coated inner surface to minimize wall heating by stray light and reduce surface losses. The central position of the gas inlet (Gi) is essential to obtain short response times using a gas flow. Only the resonator volume (here 2.8 mL) has to be replenished before an independent concentration measurement can be performed; TAC: \( \lambda/4 \) tunable air columns to suppress window signal; NF: \( \lambda/4 \) notch filter to suppress acoustic in-coupling of acoustic noise via the gas inlet. (Reproduced with permission from Ref. 30. © AIP Publishing, 1996.)

Figure 7 Two types of photoacoustic Helmholtz resonators. (a) A normal Helmholtz resonator. (Reproduced with permission from Ref. 33. © Mariusz Suchenek, 2011.) (b) A differential Helmholtz resonator. (Reproduced with permission from Ref. 34. © Elsevier, 1999.)
temperature distribution across the gas volume while the microphone operates at room temperature.\(^{(35)}\) The temperature gradient is over the long narrow tube of the resonator at which end the microphone is placed.

A way to improve the sensitivity for a specific gas is a temperature change. By increasing the temperature, the vapor pressure of, e.g. oil with low vapor pressure is increased, thereby improving the sensitivity. A Helmholtz resonant photoacoustic cell is an ideal configuration for this, since the microphone can be at room temperature (Figure 8).\(^{(36)}\)

### 3.4 Photoacoustic Detectors

#### 3.4.1 Microphones

Pressure-detection methods are widely available ranging from the large membranes as in the earliest designs of Luft\(^{(36)}\) to piezoelectric transducers operating at megahertz frequencies. Normally, for photoacoustic detection of gases, audio microphones are used. Microphones range from very small size (1-mm membrane) for hearing aid purposes behind the ear to large-size (25-mm membrane) very sensitive (1000 mV Pa\(^{-1}\)) professional microphones with a spectrally flat response to sound pressure (Bruel and Kjaer microphones). The small-size microphones (such as from Knowles) have mostly a peak in acoustic amplitude response around 1 kHz with a typical response of 10 mV Pa\(^{-1}\).\(^{(37)}\) Because of the low costs, mass-produced micro-electro-mechanical system (MEMS) microphones, commonly built into smartphones, are nowadays also incorporated in photoacoustic cells.\(^{(38)}\) Besides the fact that the latter are inexpensive, they have the advantage that they do not take up so much acoustic energy as compared to large-size microphones.\(^{(30)}\) This is important in the case of resonant acoustic cells, for which increased friction losses will lower the quality factor of the resonator and, thus, the generated acoustic amplitude.

#### 3.4.2 Quartz Tuning Fork

In gas-phase spectroscopy, the common approach is to use a resonant photoacoustic cell and accumulate the absorbed energy in the gas. However, an alternatively developed approach is to store the absorbed energy in a sensitive element. A well-suited material for this is a high-Q quartz crystal element with piezoelectric properties. Originally, these elements are mass produced and inexpensive: high-Q quartz crystals are used as frequency standard in clocks, watches, or smart phones. The mechanical and electrical properties of tuning forks (TFs) were extensively studied in relation with their application in ultrahigh resolution scanning microscopy.\(^{(39)}\) Usually, a quartz TF has a resonant frequency close to 32768 Hz. A typical TF has a \(Q\)-value of 100000 in vacuum; at normal atmospheric pressure this is lower (\(~10000\)), owing to the viscous properties of air.\(^{(40,41)}\) The mode at this frequency corresponds to a symmetric vibration (the prongs move in opposite directions), while the antisymmetric vibration is piezoelectrically inactive. This makes the TF an acoustic quadrupole, which provides good environmental noise immunity. In addition, with its narrow resonance (\(~4\) Hz) only a few frequency components can produce efficient excitation of the TF vibrations. The typical energy accumulation time at atmospheric pressure is \(~300\) ms, which is quite longer than any practical gas-filled resonator. Another property is that the gas sampling volume in between the prongs is extremely small (\(~1\) mm\(^3\)).

Nowadays there are several approaches developed to increase the absorption path length, and thus the detection sensitivity. One way is to add microresonators (mRs) to the TF (Figure 9a). This ‘on-beam’ configuration has acoustic mRs with two thin tubes aligned at micrometer distance near the TF. The laser beam will enter via the mRs, where it is critical that the laser beam does not touch the walls of the resonator; the latter will produce coherent acoustic background effects. The mRs will be acoustically coupled to the TF, and the combined acoustic behavior will result in a lower \(Q\)-factor, a slightly changed resonant frequency and an increased signal. The on-axis configuration has the disadvantage that the open-ended mRs introduce sound radiation losses. Furthermore, the gap between the prongs of the TF is \(~300\) \(\mu\)m; the inner
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Diameter of the mR has to be of the same dimensions, which limits the size of the laser beam that passes through the tubes.

An alternative configuration is the ‘off-beam’ approach, where the TF measures the pressure in the mR through a small aperture in its center. Now the mR is a single tube and its length determines the first longitudinal mode of the acoustic wave. A small slit is made in the middle of the mR for optimal acoustic coupling to the TF (Figure 9b). The off-beam-QEPAS configuration results in certain technical advantages as it facilitates the optical alignment and allows more flexibility in the selection of the dimensions of the quartz TF. In off-beam-QEPAS, the acoustic oscillations of the gas are excited in the mR by the intensity modulation induced by the externally located laser source.

3.4.3 Cantilever-type Optical Microphone

Microphones have a small gap below their membrane, which cannot be decreased below a certain level; this limits microphone sensitivity since the air flow in and out of this gap requires energy and therefore creates significant damping in the membrane. Moreover, the membrane stretches out radially, which limits the dynamical range with a nonlinear response. A cantilever-type pressure sensor has been proposed as shown in Figure 10. A thin \( t = 10 \text{ μm} \) cantilever portion moves like a flexible door, owing to the pressure variations in the surrounding gas. There is a narrow \( \Delta < 5 \text{ μm} \) gap between the thicker frame and the cantilever on three sides \( l = 6 \text{ mm}, \ w = 4 \text{ mm} \).

As the pressure varies, the cantilever only bends and does not stretch. Therefore, the movement of the cantilever’s free end can be about two orders of magnitude greater than the movement of the middle point of a tightened membrane under the same pressure variation. The displacement of the cantilever is measured via a compact Michelson-type laser interferometer (Figure 9). The laser beam is focused on the free end of the cantilever. Both arms of the interferometer are set such that there is a half of an interference fringe over each of the four photodiodes.

The abovementioned cantilever system has a large size and operates at low frequencies in a nonresonant cell with relative low SNR. Alternatively, cantilever-based resonant photoacoustic spectroscopy is proposed on top of a fiber using a small-size Fabry–Perot interferometer. The schematic structure and the image of the fiber-tip Fabry–Perot acoustic sensor head, with stainless steel shell, ceramic ferrule, and stainless steel cantilever, are shown in Figure 11. The air gap between the cantilever and the cleaved end facet of the fiber forms the Fabry–Perot cavity (length ~ 1.3 mm). The rectangular stainless steel cantilever is 1.9 mm × 0.8 mm and has a thickness of 10 μm.

3.5 Special Designs

In the past, special designs have been developed for longitudinally, azimuthally, and radially resonant photoacoustic cells even without windows. In order to improve the selectivity, the combination of the Stark or Zeeman effect with photoacoustic detection represents...
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Figure 10  (a) The dimensions of the silicon cantilever and the gap between the cantilever and the frame. (b) The set-up containing the cantilever is in principle the same set-up as the nondispersive set-up from Figure 2, but now with a cantilever detection set-up. It consists of three cells: the reference cell, the sample cell, and the photoacoustic cell. The photoacoustic cell acts as a detector and includes high concentration of the gas to be detected. The cell is divided into two parts, A and B, which are separated by the cantilever and its frame. The position of the cantilever is proportional to the pressure difference between the cell parts A and B. The displacement of the cantilever end is measured continuously with a laser Michelson interferometer. (Reproduced with permission from Ref. 43. © Elsevier, 2006.)

Figure 11  Cantilever-enhanced resonant photoacoustic spectroscopy. (a) Schematic structure. (b) Image of the cantilever sensor head. (c) Image of the stainless steel cantilever. (Reproduced with permission from Ref. 44. © Elsevier, 2018.)

an interesting solution for specific molecules such as ammonia (NH₃) \(^{48}\) and NO \(^{49}\).

Other designs are based on optical power enhancement. Since the photoacoustic signal goes proportional with the applied laser power, it is favorable to use a photoacoustic cell inside an optical cavity. This can be either by using an intracavity set-up, in which the photoacoustic cell is within the optical laser cavity or by using an external cavity. Intracavity photoacoustic set-ups are demonstrated for CO₂ and CO lasers in the mid-infrared wavelength region gaining up to 100× in power \(^{20,22,50}\) or using external cavity diode lasers and fiber lasers in the near-infrared wavelength region \(^{51,52}\).

Another approach is to use an optical cavity locked to the laser in such a way that laser power is built up in the optical cavity \(^{53,54}\). An example is shown, using quartz-enhanced photoacoustic spectroscopy and a distributed feedback QCL emitting at 4.33 μm (Figure 12). The laser optical power build-up factor is \(~500\times\), which corresponds to an intracavity laser power of 0.75 W. The
Figure 12 Schematic representation of the intracavity quartz tuning fork, enhanced photoacoustic set-up. Owing to tight locking of the laser and optical cavity, a power enhancement of ∼500 is achieved. PBS, polarizing beam splitter; λ/4, quarter-wave plate; M, mirror; MML, mode-matching lens; IM, input mirror; OC, output coupler; PI, proportional-integral controller; LM, low-frequency modulation (linear ramp); HM, high-frequency modulation (sinusoidal dither); CEU, control electronics unit. (Reproduced with permission from Ref. 53. © AIP Publishing, 2014.)

3.6 Sensitivity, Selectivity, Limitations, Interference, and Detection Limits

Laser-based absorption spectroscopy performs well in terms of sensitive and selective detection of trace gases, and it allows on-line measurements. In contrast to other sensing methods, such as mass spectrometry, the set-up can be compact, affordable, and with low maintenance costs. The high sensitivity and selectivity are due to several important factors. Firstly, the narrow linewidth of lasers gives a high spectral power density as compared to broadband light sources. Especially for cw lasers, this linewidth is typically much narrower than the molecular absorption lines. This causes the total laser emission to be attenuated by the gas sample under investigation, instead of only a small fraction, as is the case in broadband absorption. Thus, the absorption signal increases strongly due to its narrow linewidth. In addition, the selectivity improves because it enables a wavelength scan over an absorption feature. This helps to distinguish the target molecule from the interfering compounds and background signals. Selectivity enhances further by the unique spectral absorption spectrum of each molecule, which corresponds to different rovibrational transitions of the molecule. Spectroscopic gas detection probes the internal structure of the molecule, whereas other techniques such as mass spectrometry only assess a global property of the investigated compound.

In the infrared fingerprint wavelength region (2.5–25 μm) small molecules have their characteristic strong absorption lines (Figure 13). Combined with highly sensitive spectroscopic methods, gases can be detected at trace levels below the parts-per-billion-volume range (1 ppbv = 1 x 10^9 mol/mol). A disadvantage of laser-based spectroscopy is that larger molecules have more vibrational modes (3N-6, with N the number of atoms in the molecule) and a smaller rotational constant. At room temperature, this results in broad structures of overlapping rotational lines with much lower spectroscopic selectivity.

Initially, molecular CO2 and CO lasers dominated molecular detection of gases in the mid-infrared due to their high-power (photoacoustic signal is proportional to the laser power) and wide wavelength coverage. In the past decades, the selective detection of molecular gases improved strongly for a wide range of gases with the development of QCLs and OPOs. The invention of the QCL made it possible to operate current-driven diode-like lasers at room temperature in the mid-infrared wavelength region from 3.5 to as long as 19 μm. The first cw singly-resonant OPOs, suitable for trace gas detection, were developed in 1996; they contained a quasi-phase-matched PPLN crystal with a long interaction length (several centimeters) to lower the threshold for operation.
In the near-infrared wavelength region, photoacoustics is not favorable for trace gas detection. In this region there are mainly weak vibrational overtone absorption bands, in comparison to the (100–1000 times) stronger fundamental bands in the mid-infrared region. However, other trace gas sensing methods, based on direct absorption spectroscopy, are successfully used in this region (e.g. cavity ring-down spectroscopy and cavity-enhanced absorption spectroscopy).\(^{56,57}\) They profit from the high-quality commercially available telecom lasers, the long (cavity-enhanced) absorption path lengths (mirrors with extreme high reflectivity: >99.99%), and the excellent detectivity \((D^*)\) of the available detectors to detect a small \(\Delta P\) (Equation 1). In addition, telecom lasers have mostly low power output; therefore, photoacoustics is not competitive. In the mid-infrared wavelength region, this advantage does not exist, because of the less well-developed infrared mirrors and less-sensitive optical detectors.

In order to have a maximum SNR, one has to take into account the noise contribution. The theoretical minimum acoustical noise results from random pressure fluctuations and their frequency distribution due to Brownian motion. The total power of these pressure fluctuations is constant, but the noise spectrum depends on the \(Q\)-value of the acoustical resonance of the photoacoustic cell; a high \(Q\)-value will significantly amplify noise power at these resonances. However, often this Brownian noise level is below what is produced by other noise sources, such as electronic amplifier noise and external acoustical noise from the surroundings; their power decreases with increasing frequency. It is then advantageous to utilize a resonant cell to improve the SNR. The resonance frequency might be chosen such that contributions from Brownian noise and amplifier/external noise become comparable. At resonance, external acoustical noise within the cell will be amplified at a high \(Q\)-value. Here acoustical shielding helps, that is a proper cell wall construction (massive), material choice for a high acoustic impedance (such as brass), and good design of in- and outlet ports are required. For the latter, \(\lambda/4\) notch filters (\(\lambda\) the acoustical wavelength) are positioned inline with the gas in- and outlet (Figure 6). Several types of microphones are used for a photoacoustic resonant cell, but the most used are hearing aid microphones, which are mass produced, small, and relatively cheap.\(^{37,54}\)

By definition, noise components do not possess a fixed phase relation with the periodical modulation of the light.
intensity. However, external perturbing sources may have a fixed phase relation, for example the directly generated acoustical sound caused by amplitude modulating the light beam. They must be minimized in the same way as the external acoustical noise. A more serious problem is formed by the photoacoustic background signal. Absorption of the light beam in the window material or light scattered/reflected from the resonator wall causes a signal at the frequency of the modulated light beam. In resonant cells, using λ/4 tubes next to the windows can diminish window signals. These tubes, placed perpendicular to the resonator axis close to the windows, are tuned to the resonator frequency and act as notch interference filters for the window signals (Figure 6). Influence of scattered light on the photoacoustic background signal can be minimized by use of highly reflecting, polished resonator wall material with a good thermal conductivity. In the case of infrared light, a polished gold-coated copper wall of the acoustical resonator has been found to work satisfactorily.

Another way to diminish the photoacoustic background signal is to frequency modulate (FM) the laser light over the molecular absorption line. As the wall/window material will have broad absorption features, they will hardly contribute to the 1f of 2f generated signal of the molecular absorption line.(58,59)

3.6.1 Kinetic Cooling Effect

Using infrared absorption spectroscopy, the absorption process involves vibrational transitions. For photoacoustic spectroscopy, the increase in vibrational energy is transferred by collisional relaxation processes to translational energy, causing the gas to eventually be heated, generating a pressure increase. In the case of molecules with many low-lying energy states (such as H2O), this relaxation process is rapid. When the relaxation process becomes slow, as compared to the modulation frequency of the light, the generated photoacoustic signal changes in phase and decreases in amplitude, thereby severely affecting the linearity and sensitivity of the photoacoustic signal for trace gas detection.(60–63)

In the atmosphere, N2 has a long vibrational lifetime of its first excited vibrational mode (≈1 ms at 1 atmosphere at ν1 = 2200 cm⁻¹). When atmospheric CO2 is detected using a CO2 laser in the mid-infrared wavelength region (9–11 μm), CO2 will absorb via a hot-band absorption and is excited to the ν3-vibrational level (Figure 14). This level is almost resonant with the first vibrational level of N2. Since N2 is much more abundant than CO2, all the vibrational energy will go into N2. Under atmospheric conditions the absorbed energy by CO2 will only slowly be converted into a temperature and pressure increase of the gas. Using kilohertz modulation of the laser beam, a phase shifts occurs in the generated photoacoustic signal. N2 is not unique; similar effects can be observed with oxygen and CH4.(64) Oxygen has a near-resonant vibrational level (1554 cm⁻¹) with the lowest vibrational level of methane; only 170 collisions are needed to transfer energy from methane to the vibrational mode of O2.(65) The average number of collisions required for O2 to relax to the ground state is 8.3 × 10⁷. The much larger number density as compared to CH4 creates a buffer of vibrational

![Figure 14](Image)

**Figure 14** Vibrational energy level diagram for atmospheric species important in the transfer of energy absorbed by CO2 at 10.6 μm. The indicated relaxation times have been determined for the 1962 US Standard Atmosphere at sea level, assuming a relative humidity of 30%. Note that the energy is given in Kelvin, 1 K = 0.695030 cm⁻¹. (Reproduced from Ref. 60. © Optical Society of America, 1971.)
energy leading to an effective transient cooling of the translational degrees of freedom. Owing to a high photoacoustic modulation frequency (1010 Hz), we observed this transient cooling by O2 as an amplitude decrease and a phase change relative to the signal caused by the same amount of CH4 in N2.

Addition of H2O or SF6 molecules (notorious relaxers) to the gas under investigation can reverse the situation. An example is shown with the strong rotational–vibrational absorption band of CO2 at 4.23 μm. To overcome the slow vibrational relaxation of the excited CO2 levels, 4% of SF6 gas was added to the atmospheric mixture (Figure 15). In this way, it was possible to detect CO2 down to 7 ppbv using 20 mW of the OPO light.

3.6.2 Interference of Other Gasses

In other cases, limitations are caused by the presence of a complex mixture of gases to be investigated. Gases spectroscopically interfere if molecular absorption lines are close to each other. The most abundant infrared absorbing gases are water and carbon dioxide. To overcome such interferences, detection can be performed at reduced pressure, thereby reducing the pressure broadening. With the nowadays tunable lasers, one can chose the appropriate wavelength to minimize the effect of other gases. An example is given in Figure 16 (67) When measuring biological samples such as plants, seeds, bacteria, or human breath, attention has to be paid to interfering gases such as water and CO2. To detect hydrogen cyanide (HCN) at low concentration in exhaled breath, an optimal wavelength has to be found in the wavelength region around 3287 cm\(^{-1}\). To estimate the interference of HCN absorption lines with water and CO2 absorption lines, the ratio is calculated between the absorption of 10 ppbv of HCN and the sum of absorption coefficients of 1% water and 5% CO2 referring to the HITRAN database (16) (Figure 16a). This ratio helped to determine the best spectral regions for detecting HCN from biological samples. It plays a role of a first step of an analysis to limit the wavelength choice. The full analysis requires consideration of a few other factors, such as interfering gases in a gas mixture, concentrations of compounds, pressure, absolute intensity of a particular absorption line, and availability of a laser source. A few of the spectral regions are plotted in the panels of Figure 16, where the P8 transition in the ν1 band of HCN, at 3287.247603 cm\(^{-1}\), was found to be the best for our biological experiments, because it has less interference with CO2.

Gases can also be separated by gas chromatographic methods, selective trapping inside a cold trap (e.g. water), (50) or by a specific chemical reaction (e.g. removal of CO2 by making KOH to react with K2CO3, and water with CaCl2). In most cases, a small amount of the interfering compound remains present. To address this issue, a multicomponent analysis is necessary.

Also, the gas under investigation can prevent stable and reliable long-term measurements. To perform a proper sampling, it is important to avoid any metal parts in the gas flow system from the sample to the photoacoustic detection cell; wall adsorption on metal parts significantly reduces an initial gas mixing concentration. The photoacoustic cell is normally made out of metal, but can be coated with Silcosteel coating to reduce adsorption of polar gases.

4 APPLICATIONS

4.1 Atmospheric Applications

Early attempts were made to measure stack gas emissions from power plants with laser photoacoustics. Owing to the high amount of NO and NO2 compounds in the emissions, they have a significant contribution in photochemical smog formation and acidification of the soil. To reduce this, NH3 is added in the exhaust gas toward the chimney. Using a voluminous catalyst, NOx reduction (within the stack gas) takes place. In order to check the performance and to avoid an excess of ammonia...
injection, the ammonia concentration in the chimney is monitored. For this, a CO$_2$-laser-based photoacoustic detection system was successfully applied for in situ monitoring of ammonia concentrations.$^{(68)}$ Owing to the difficulty, that is hostile environment halfway up the chimney (vibrations, temperature fluctuations, etc.), concessions have to be made as to the sensitivity of the apparatus. With a nonresonant photoacoustic cell at $125^\circ$C, a detection limit of 1 ppmv NH$_3$ was achieved in a multicomponent gas mixture containing 10–15% CO$_2$.

Another example is the mobile system for field campaigns by Sigrist et al. Installed in a small trailer, the system has been operational for years and has been applied for several field campaigns in urban and rural environments.$^{(24,69–71)}$ For example, as part of an atmospheric pollution measurement campaign, they performed in situ measurements of NH$_3$, C$_2$H$_4$, and CO$_2$ concentrations at the exit of a freeway tunnel with a time resolution of 1 min over a period of 5 weeks. Peak concentrations were observed at 600 ppbv (NH$_3$), 400 ppbv (C$_2$H$_4$), and 1000 ppmv (CO$_2$). Owing to these multicomponent gas mixtures, cross-sensitivities in the absorption coefficients are induced, and as a result detection limits are higher, as compared to those based on extrapolation from larger quantities of trace gases in a clean buffer gas. A mathematical analysis of the photoacoustic spectra of multicomponent mixtures is based on the weighted least squares fit of the measured spectra with spectra from pure compound spectra. The latter spectra are separately taken from trace gas mixtures in pure nitrogen or air.

Numerous practical applications, in industrial process control and environmental monitoring, require sensitive and selective concentration measurement over long time periods by compact and automatic monitoring instruments. This became available with the development of tunable diode, quantum cascade, and other compact lasers systems, resulting in the development

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**Figure 16** (a) Ratio between 10 ppbv of HCN and a sum of 1% of water and 5% of CO$_2$ for a pressure of 200 mbar in the wavelength range 3200–3400 cm$^{-1}$. (b–d) Simulated spectra at a 200 mbar pressure inside the photoacoustic for 1% of water (black-dashed line), 5% of CO$_2$ (red-dotted line), and 10 ppbv of HCN (blue solid line). (Reprinted with permission from D. D. Arslanov, M. P. P. Castro, N. A. Creemers, A. H. Neerinck, M. Spune, I. Mandon, S. M. Cristescu, P. Merkus, and F. J. M. Harren, “Optical parametric oscillator-based photoacoustic detection of hydrogen cyanide for biomedical applications,” *Journal of Biomedical Optics* **18** (2013). Copyright 2013 SPIE.$^{(67)}$)
of compact and reliable photoacoustic instruments. Very compact laser-based TF photoacoustic sensors have been demonstrated for detection of chemical species, such as NH₃, NO, CO₂, N₂O, CO, CH₂O, and C₃H₆O, with a record detection limit of 50 parts per trillion for SF₆, corresponding to a NNEA value of $2.7 \times 10^{-10}$ W cm⁻¹ Hz⁻¹/₂. For these publications, see, e.g., Refs. 32, 40, 41, 73, 74 and references therein.

For the detection of NO₂, photoacoustic cell functions at its best in the visible or infrared wavelength regions, where it has a low-lying electronic transition in the blue-violet region around 400 nm, next to its vibrational absorption band in the infrared. A sub-ppbv detection limit has been achieved with external cavity QCLs at 6 μm in combination with photoacoustic detection. A much cheaper, smaller, and cost-effective approach is to use blue LED or blue diode lasers. The latter is based on the implementation of low-cost components, i.e. a mass-produced blue diode laser and a standard MEMS microphone, which is commonly built into smartphones. A photoacoustic cell design was realized by means of 3D printing (Figure 17). The detection limit was determined to be 33 pptv NO₂ and the NNEA $7.0 \times 10^{-10}$ W cm⁻¹ Hz⁻¹/₂.

Ammonia is the third most abundant nitrogen compound in the atmosphere and plays a significant role in cloud and rainwater chemistry. Typical ammonia sources include livestock, fertilizers, soils, forest fires, humans, animals, oceans, industry, and traffic. The main emission source is the use of animal manure and fertilizers for agricultural soils (responsible for more than 80% of the total ammonia emission). In Figure 18, a QCL-based photoacoustic set-up is shown with the QCL and power meter mounted into the photoacoustic cell. This commercial photoacoustic system is able to detect ammonia down to a concentration of 2 ppbv in realistic conditions.

Another laser-based photoacoustic instrument was developed and used for aircraft measurements of ethene from industrial sources near Houston (Figure 19). This instrument provided 20-s measurements with a detection limit of $\sim 0.7$ ppbv.

![Figure 17](image1.png)

![Figure 18](image2.png)

Ethene (ppbv)

Emission (kg h⁻¹)

Wind direction

Houston

Houston ship channel

Mt. Belvieu

Bayport

Galveston bay

Texas city

Sweeney

Freeport

Chocolate bayou


instrument were compared with gas chromatographic measurements, which agreed within 15% on an average. Ethene fluxes from a chemical complex near Houston could be quantified during 10 different flights. The average measured fluxes were one order of magnitude higher than the regulatory emission inventories indicate.

4.2 Detection of Chemical Warfare Agents and Explosives

Over the past decades, the global rise in terrorism and its threats against public places (markets and airports) has increased the awareness for the development of sensitive detectors for the early detection of the presence of chemical warfare agents and explosives, such as Sarin affecting the nerve system. Such chemicals have a large amount of rotational and vibrational modes that are populated at room temperature; therefore, these molecules have no spectrally resolved lines, but broadband absorption structures (Figure 20). For such broadband structures, broadly tunable lasers are needed. CO₂ lasers in combination with photoacoustic spectroscopy are used for this detection of vapors. However, these laser sources are only line tunable, and it is difficult to access the strong absorption features. The development of QCLs can fulfill these criteria, as they have continuous tunability and can be designed for specific wavelength regions ranging from 3 to 20 μm. In an external cavity configuration they have a wide wavelength coverage (~300 cm⁻¹) at high power (>100 mW up to several Watt). However, high sensitivity alone is not sufficient. Such a sensor must have very few false alarms to avoid unacceptable social and economic disruptions.
ENVIRONMENT: TRACE GAS MONITORING

Figure 20  Spectral absorption features of a number of chemical warfare agents in the 9–11.5 \( \mu \text{m} \) region, within the lower level the positions and relative power levels of the \(^{13}\text{C}_2\text{O}_2\) laser output on the lasing transitions as a function of the wavelength. (Reproduced with permission from Ref. 79. © AIP Publishing, 2006.)

The problem of interference rejection is severe because of the broad absorption features of many chemical warfare agents. In normal indoor or outdoor environments, hundreds of gases are present, of which a few dozen need special consideration because of their ambient concentrations, absorption magnitudes, and spectral overlap.\(^{79}\)

4.3 Biological and Agricultural Applications

4.3.1 Plant Physiology

For a long time, plants were known to emit ethylene \((\text{C}_2\text{H}_4)\); it is considered a gaseous phytohormone regulating various growth and development processes, starting from seed germination through growth and flowering, until fruit ripening and plant senescence, synergistically or antagonistically with other hormones.\(^{81,82}\)

The biosynthesis in plants is well understood, leading from the amino acid methionine over two intermediates, \(\delta\)-adenosylmethionine and amino-cyclopropane-carboxylic acid, to ethylene. Ethylene is produced by plant tissue as a response to many external factors, such as pathogen attack,\(^{83}\) herbivorous predation,\(^{84}\) and abiotic environmental factors including flooding,\(^{85}\) chemical exposure,\(^{86}\) day length and light intensity,\(^{87}\) temperature,\(^{88}\) or nutrient availability.\(^{89}\)

Ethylene emissions may vary according to the plant species, organ type (e.g. root, leaf, and flower), and developmental stage of the plant. It is demonstrated that ethylene can stimulate fruit ripening even at low ppbv levels.\(^{90}\) Therefore, it is of paramount importance to monitor and control the ethylene emission in growth chambers, greenhouses, and storage facilities to optimize fruit freshness. Controlled atmosphere was developed to allow longer storage periods and, subsequently, to provide a wide variety of fruits to the consumers over the entire year. Apart from the agricultural- and industrial-related involvement of ethylene in controlling fruit quality, a lot of effort has been dedicated to understanding the physiological mechanism of ethylene biosynthesis, action, and perception in plants. In spite of great achievements at both the plant’s molecular and physiological levels, many ethylene-related plant events remain unrevealed, mainly due to a lack of fast and sensitive ethylene detection.

Hence, there is an increasing demand for simple, affordable, and reliable ethylene sensors that could be used in conjunction with equipment for controlling ethylene concentrations. With laser-based photoacoustic detection, the dynamics of many processes that take place in plants become easily visible. For example, ethylene released by Arabidopsis displays a circadian rhythm (high emission during the light and low emission during dark) with a peak in the mid-subjective day. When the plants were grown for 6 days in a succession of light (16h) and dark (8h) and afterward were kept in continuous light for
several days, they showed an ethylene pattern as would follow the light–dark periods (Figure 21). 

Figure 21 Influence of day length on ethylene production in Arabidopsis. Seedlings were grown for 6 days in 16 h light and 8 h dark and then tested for ethylene emission during one light–dark cycle followed by constant light. Ethylene released by Arabidopsis displays a circadian rhythm with a peak in the mid-subjective day.

One of the major environmental factors influencing crop productivity is flooding. Tolerant species often possess ‘escape’ mechanisms such as fast underwater growth that minimizes the duration of total submergence. However, at early vegetative stages, even in ‘deep-water’ types of rice, such escape is precluded by a lack of sufficiently vigorous shoot elongation for resurfacing. Survival of submergence under these circumstances depends on intrinsic physiological and biochemical tolerance. Screening of cultivars is needed by plant breeders, agrotechnology, and biotechnology to achieve sustainable improvements in the productivity of rice farming in the rain-fed lowland of Southeast Asia. Submergence is not an easily quantified stress compared with, for example cold, heat, and pollution, since it cannot be assessed by one simple analysis. This is because it involves exclusion and entrapment of several key gases and interference with illumination. Normal rates of respiration and photosynthesis are affected; differences in submergence tolerance are reflected also in a different reaction to low oxygen concentrations. Precise measurements of fermentation rates can result in a powerful tool to shed some light on submergence stress. Fermentation in plant tissue was studied by the use of photoacoustic techniques, through detection of ethanol and acetaldehyde. It was shown that young rice seedlings of various species show different degrees of tolerance toward submergence, which is expressed by different fermentation rates under anaerobic and submergence conditions.

4.3.2 Postharvest Physiology

It is estimated that globally 33% of the edible parts of food produced for human consumption gets lost or wasted. Worldwide, 1.6 billion tons of fruit and vegetables are produced, from which 120 million tons are lost during the postharvest process, i.e. losses due to spoilage and degradation during handling, storage, and transportation between farm and distribution. Storage involves strict protocols with respect to timing of harvest and the gradual establishment and maintenance of the storage conditions. Often it involves storage at low temperature, decreased oxygen, and increased carbon dioxide concentrations. During or after storage, physiological or pathological disorders may develop, which can greatly diminish the commercial value of the fruits, owing to spoilage or quality classification downgrading. The optimization of the storage conditions and timing in order to maximally preserve the quality is a challenge, owing to restricted access to the products for quality inspection under such strict regimes. In addition, to enable decision-making, it is important to have relevant information about the status of the stored products. Information about the actual ripening stage and the possible occurrence of fungal infections may influence the decisions about the best moment in time to open stores and sell the fruit.

The respiration quotient (ratio between CO$_2$ produced and O$_2$ consumed) indicating aerobic or anaerobic (fermentation) metabolism is an important parameter that can serve for adjusting the oxygen concentration in the storage room. Other important volatiles released by stored products include ethylene (marker for ripening), ethane (indicator of damage), ethanol, acetaldehyde, and ethyl acetate (markers for fermentation), while methanol and acetone may serve as rotting process indicators. More specifically, the development of fungal infections (potentially dangerous for the consumer’s health via mycotoxins) during storage may be detected by rotting volatiles in combination with low levels of fermentation volatiles. Therefore, the continuous monitoring of such volatiles is important not only for food quality but also for food safety control. The noninvasive nature of laser-based trace gas detection renders it suitable for applications in this field of postharvest physiology. Moreover, the high sensitivity combined with fast analysis allows one to study an individual piece of fruit so that metabolic activity may be followed in real time.

4.3.3 Microbiology

The growth of all organisms depends on the availability of mineral nutrients, and nitrogen is one of the most required in many biological reactions. Although the earth’s atmosphere contains nearly 80% of nitrogen...
gas, this is unavailable for use by most organisms, being
an inert molecule. In order for nitrogen to be used for
growth, it must be ‘fixed’ (combined) in the form of
ammonium or nitrate ions. This conversion process is
known as nitrogen fixation and is exclusively performed
by prokaryotes (bacteria) using an enzyme complex
called nitrogenase.\(^{(97)}\) Acetylene reduction is the most
widely used method for measuring the nitrogenase
activity.\(^{(98)}\) It is based on the nitrogenase property to
reduce compounds with a triple bond. Thus, by reducing
nitrogen to ammonia, the nitrogenase reduces acetylene
to ethylene. Both these gases can be measured with high
sensitivity by gas chromatography with flame ioniza-
tion detection. However, owing to its higher sensitivity
and fast time response (about 20 s), laser photoacoustic
spectroscopy offers the advantage of monitoring small
changes in the nitrogenase activity of low amounts of
biomass in real time.\(^{(99)}\) The on-line monitoring allows
measurements under constant conditions, which elimi-
nates artifacts caused by changes in the concentrations
of \(\text{O}_2\) or \(\text{CO}_2\) due to respiration or photosynthesis during
incubation. Changes in light intensity and temperature
induce fast response in the nitrogenase activity. Knowing
the level of saturation of the enzyme at different tem-
peratures and light is important when rates of acetylene
reduction are converted to rates of nitrogen fixation (Figure 22).

4.3.4 Entomology

Methane has been recognized as one of the principal
greenhouse gases, next to \(\text{CO}_2\). Its estimated contribu-
tion to the enhanced greenhouse effect varies between
15% and 20%, depending on the time window for which
the calculation is made. Natural sources are responsible
for the major part of the global methane flux.\(^{(100)}\) Some
arthropods (i.e. millipedes, cockroaches, termites, and
scarab beetles) are believed to contribute up to 25% of
the total budget.\(^{(101)}\) Gas chromatography allows
measurement of methane release of single animals only
after incubation for several hours. Consequently, these
measurements cannot provide information about the
dynamic character of the gas emission. Infrared absorp-
tion measurements featuring fast response time permitted
observation of the dynamics of \(\text{CO}_2\) emissions. Besides
\(\text{CH}_4\) and \(\text{CO}_2\) emissions from insects, water vapor release
has been the subject of many studies. Information about
water loss dynamics in insects is based on theoretical
modeling, sensitive weighing, and relatively slow direct
water vapor measurements.\(^{(102)}\) Using laser photoacoustic
detection, cockroaches at rest show a regular breathing
pattern to optimize oxygen uptake and reduce water
loss. Respiration patterns of cockroaches and beetles
have been recorded in which microbiologically produced
methane was found to be co-emitted with \(\text{CO}_2\) and water
vapor (Figure 23).

Combining an OPO with photoacoustic spectroscopy,
\(\text{CO}_2\) emissions even from small insects could be
detected. For this the OPO was made tunable in the
3.9–4.8 \(\mu\)m infrared wavelength region, covering the
strong rotational–vibrational absorption band of \(\text{CO}_2\) at
4.23 \(\mu\)m. With this system, it was possible to detect \(\text{CO}_2\)
with a sensitivity of 7 ppbv using 20 mW OPO power.
They demonstrated in real time the \(\text{CO}_2\) emission in
exhaled air of a single ant (\textit{Lasius niger}) and individual
fruit flies (\textit{Drosophila melanogaster}, see Figure 24).\(^{(66)}\)

4.4 Human Health, Noninvasive Breath Analysis

Humans exhale hundreds of gases, including inorganic
compounds (e.g. \(\text{NH}_3\), \(\text{NO}\), and \(\text{H}_2\text{S}\)) and volatile organic

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**Figure 22** Response of cyanobacteria \textit{N. spumigena} (see photo) to change of temperature from 10 to 37 \(^\circ\)C under light conditions. Significant instability in the nitrogenase activity is observed at 35 \(^\circ\)C, leading to a short inhibition tendency at 37 \(^\circ\)C, followed by a drastic decrease.
compounds (VOCs, e.g. acetone), arising from their normal body metabolism.\(^{(103-105)}\) Human breath also contains exogenous compounds that originate from food and beverages or from current or previous environmental exposures.\(^{(106)}\) Since ancient times some diseases have been recognized by their associated odor.\(^{(107)}\) Uncontrolled diabetes produces a sweet, fruity odor; advanced liver diseases entail a musty, fishy reek; failing kidneys bring about an urinelike smell; and a lung abscess can be brought to light by its putrid stench. After Pauling’s breakthrough in 1971,\(^{(108)}\) modern breath analysis has connected these odors with specific gas analytes (biomarkers) or a profile of VOCs. Although many exhaled compounds potentially reflect the physiological and pathophysiological conditions related to various diseases, only some VOCs have been established as biomarkers.\(^{(109)}\) Several methods are currently employed for exhaled volatiles detection, among which mass spectrometry is the most widely used analytical tool.\(^{(110)}\)

Next to analytical tools, there is a strong need for miniaturized devices, which are affordable, accurate, and user-friendly, providing a fast response, preferably in real time. This is where the strength is of optical methods: specific, reliable, quantitative real-time analysis of single analytes, and without the need for frequent calibration.

A list of representative molecules of medical interest determined with laser-based spectroscopic methods is listed elsewhere.\(^{(110)}\) Depending on the specific experimental set-up, laser-based measurements can be done in real time (subsecond time resolution and resolving individual breath cycles) or near real time.

Owing to its high sensitivity, laser photoacoustics allows single breath collection from a small sampling volume (few hundred milliliters) with no preconcentration steps needed. An early example of using laser photoacoustics for breath analysis is the investigation of the effect of UV radiation on the human skin. Under stress conditions (e.g. ionizing radiation, toxic chemical substances, and diseases), the production of free radicals in the body is significantly increased. Subsequently, the capacity of the free radical scavengers in the body is overloaded, and a chain of chemical reactions is activated.\(^{(111)}\) This leads ultimately to cell membrane damage (i.e. lipid peroxidation and oxidation of fatty acids in cell membrane) that plays an important role in the aging processes and pathogenesis of some diseases. The cell damage is accompanied by the production of small hydrocarbons such as ethane, pentane, and ethylene that can be easily measured, also with photoacoustics.\(^{(112,113)}\) This investigation was recently extended to a clinical setting, with

![Photoacoustic Spectroscopy](image-url)
the assessment of lipid peroxidation by expired ethylene during cardiac surgery.\(^{114}\) Patients were undergoing aortic or mitral valve surgery requiring cardiopulmonary bypass and off-pump coronary artery bypass surgery. The study revealed for the first time the real-time signatures of the surgical response triggered by oxidative stress including lipid peroxidation (Figure 25). This innovative approach has demonstrated the significant contribution of diathermy to overall oxidative stress and identified increased ethylene associated with regional myocardial ischemia on an individual basis. It can be concluded that sensitive, totally noninvasive, and real-time analysis of lipid peroxidation using breath ethylene is feasible in the clinical and perioperative setting.\(^{115}\)

Cystic fibrosis (CF) is a multisystem disease, leading to chronic respiratory infections that result in progressive loss of lung function and diminished life expectancy. \textit{Pseudomonas aeruginosa} is one of the most common pathogens causing these infections. The presence of this opportunistic bacterium is associated with a high morbidity and mortality rate.\(^\text{116,117}\) Initially, the bacterium can often be eradicated with aggressive antibiotic treatment. However, over time the phenotype changes, complicating eradication. To detect and monitor

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**Figure 24** (a) Real-time CO\(_2\) emission of a small ant (\textit{Lasius niger}, weight 3.7 mg). Analysis of the ants’ respiration shows a periodic release of CO\(_2\), on an average every 90s. (b) CO\(_2\) release of a fruit fly (\textit{Drosophila melanogaster}, weight 1.4 mg). The comparison of the CO\(_2\) trace from the fruit fly with the background (without fly) shows that the CO\(_2\) release does not drop to zero. The accuracy of the CO\(_2\) detection shows that the CO\(_2\) peaks vary in amplitude and frequency. (Reproduced with permission from Ref. 66. © Springer-Verlag, 2006.)

**Figure 25** Intraoperative, real-time monitoring of ethylene measured in patients undergoing off-pump coronary artery bypass surgery. (a) Example of continuous monitoring during the entire operation. At \(t = 0\) h, the patient was connected to the sampling line; DT, diathermy electrocautery with high-frequency electric currents. (b) Example of a grafting procedure. The high-resolution peaks are associated with ethylene induced by lipid peroxidation during the reperfusion events. (Reproduced with permission from Ref. 114. © American Physiological Society, 2014.)
PHOTOACOUSTIC SPECTROSCOPY IN TRACE GAS MONITORING

P. aeruginosa, it is needed to screen patients frequently for colonization, and to start with aggressive eradication therapy. The current ‘golden standard’ for detection of P. aeruginosa is a sputum culture. However, young CF patients are not able to expectorate adequate samples. Alternatives have therefore been sought and include invasive bronchoscopy, non-specific chest X-ray, or unreliable cough swabs methods. For this reason, there is a need for a quick, patient friendly, reliable, safe, and sensitive method to diagnose P. aeruginosa infection in an early stage. The ability of P. aeruginosa to synthesize HCN can be the base of this diagnosis. Cyanogenesis or HCN synthesis occurs only in a few bacterial species, including P. aeruginosa.

Mid-infrared OPOs are considered among the most useful tools for sensitive laser photoacoustic gas sensing, owing to their high-power (Watt-level), wide tuning range, and ease of tunability. Here, such a light source was successfully applied for the detection of HCN in exhaled breath of CF patients. In high concentrations, HCN is toxic, but it may also originate endogenously (in small amounts), from pathogens or ingestion of food.

5 COMPARISON WITH OTHER SPECTROSCOPIC METHODS IN TRACE GAS MONITORING

Fast and sensitive trace gas detection is not exclusively reserved for photoacoustics. In general, all spectroscopic techniques are able to monitor gas absorptions on a subsecond timescale. However, depending on the type of application not all techniques possess a high sensitivity. The sensitivity of a gas absorption measurement can be enhanced in two ways: either by increasing the absorption path length or by increasing the SNR.

Using direct absorption spectroscopy over short distances the most abundant species can only be detected (such as CO₂ and water vapor). This can be improved using multipass cells, thereby increasing the path length to several tenths of meters, achieving sub-parts-per-million gas concentrations levels. Direct absorption will have minimal detectable absorption (MDA) of ~10⁻². MDA is defined as:

\[ \text{MDA} = \frac{\alpha_{\text{min}}}{B} \]

with \( B \) the detection bandwidth (Hz), with the minimum absorption, \( \alpha_{\text{min}} = \Delta I/I \), equivalent to the ratio of laser intensity noise \( \Delta I \) and laser intensity \( I \). The detection bandwidth is important, as it normalizes the integration time over the measurement. Wavelength modulation spectroscopy (WMS) improves the MDA to 10⁻⁵ to 10⁻⁶, because of the high modulation frequencies, reducing the noise on the intensity detection.

Trace gases in the open air can be very well studied along long light paths, rendering low detection limits. To normalize and to be able to compare methods over path lengths, the noise equivalent absorption sensitivity (NEAS) is defined:

\[ \text{NEAS} = \frac{\text{MDA}}{L} = \frac{\alpha_{\text{min}}}{L \sqrt{B}} \]

Cavity ring-down spectroscopy and integrated cavity output spectroscopy make use of a high finesse cavity to have a very long path length (up to kilometers) in a cavity with a small footprint, thanks to the use of high reflective mirrors and sensitive infrared detectors. Thanks to the long path length the NEAS can reach, 10⁻¹⁰ to 10⁻¹¹, although the MDA stays at the level of 10⁻⁶ (Table 1).

Laser-based photoacoustic detection has the advantage that it is background free: it is not relying on a decrease of the transmitted light (and thus the intensity noise), but on an increase from a zero baseline, i.e. on a collisional release of energy after absorption. As such the MDA will already be in the 10⁻⁸ Hz⁻¹/² region. At small absorptions, the photoacoustic signal is linear with the laser power (Equation 1); to compare photoacoustic sensitivities, the MDA is normalized on the laser power instead of the path length: the NNEA with typical values of 10⁻⁵ W cm⁻³ Hz⁻¹/². Using a laser power of 1 W and having an absorption path length in the photoacoustic cell of 10 cm, the NEAS is at the 10⁻⁹ cm⁻³ Hz⁻¹/². Another background-free and therefore strongly competitive

<table>
<thead>
<tr>
<th>Method</th>
<th>( \alpha_{\text{min}} ) (cm⁻¹)</th>
<th>( L ) (cm)</th>
<th>( t ) (s)</th>
<th>MDA (Hz⁻¹/²)</th>
<th>NEAS (cm⁻³ Hz⁻¹/²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct absorption</td>
<td>4 × 10⁻²</td>
<td>5000</td>
<td>10</td>
<td>10⁻²</td>
<td>2 × 10⁻⁸</td>
</tr>
<tr>
<td>Wavelength modulation</td>
<td>2 × 10⁻⁴</td>
<td>5000</td>
<td>10</td>
<td>5 × 10⁻⁵</td>
<td>10⁻⁹</td>
</tr>
<tr>
<td>Cavity-enhanced methods: CRD/ICOS</td>
<td>1 × 10⁻⁵</td>
<td>50000</td>
<td>10</td>
<td>2 × 10⁻⁶</td>
<td>5 × 10⁻¹¹</td>
</tr>
<tr>
<td>Photoacoustic (PA) (1 W power)</td>
<td>4 × 10⁻⁸</td>
<td>10</td>
<td>10</td>
<td>10⁻⁸</td>
<td>10⁻⁹</td>
</tr>
</tbody>
</table>

The minimal absorption \( \alpha_{\text{min}} \) is normalized on the bandwidth (B), which has the relation with the integration time \( t = 1/B \), using the Nyquist criterion. Measurement time and path length (L) are typical laboratory values to achieve \( \alpha_{\text{min}} \). Photoacoustic values are converted to NEAS using 1 W of laser power (see text).
ENVIRONMENT: TRACE GAS MONITORING

The technique is LIF. LIF is extremely sensitive owing to the high collection efficiency of photomultipliers; they can be applied locally within a small gas volume. LIF and laser photoacoustics are complementary in energy release. The advantage of LIF is that it can also detect free radicals (e.g. OH) with relatively low laser powers. A restriction of LIF is the lifetime of the excited levels. As stated in Section 1, the competition between collisional relaxation and radiative decay restricts LIF mainly to the visible and the UV parts of the electromagnetic spectrum.

ACKNOWLEDGMENTS

The authors wish to thank J. Reuss for the helpful discussions. Also, the authors thank F. Bijnens, H. de Vries, S. Persijn, T. Groot, E. Santos, I. Boamfa, M van Herpen, B. Moeskops, M. Steeghs, A. Ngi, E. Crespo, D. Arslanov, D. Marchenko, D. Samudrala, R. Centeno, Y. Jin, A. Neerinx, S. te Lintel Hekkert, L.J. Laarhoven, P. Brown, and J. Mandon for their experimental support and C. Sikkens for technical assistance. Finally, they would like to thank the Dutch Science foundation, Dutch Technology Foundation, Dutch Royal Academy of Science, Province of Gelderland, INTERREG North-West Europe, and the European Union for their continuous financial support via various programs.

ABBREVIATIONS AND ACRONYMS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>CF</td>
<td>Cystic Fibrosis</td>
</tr>
<tr>
<td>cw</td>
<td>Continuous Wave</td>
</tr>
<tr>
<td>FM</td>
<td>Frequency Modulation</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transformed Infrared</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>HCN</td>
<td>Hydrogen Cyanide</td>
</tr>
<tr>
<td>ICL</td>
<td>Interband Cascade Laser</td>
</tr>
<tr>
<td>LED</td>
<td>Light-emitting Diode</td>
</tr>
<tr>
<td>LIF</td>
<td>Laser-induced Fluorescence</td>
</tr>
<tr>
<td>MDA</td>
<td>Minimal Detectable Absorption</td>
</tr>
<tr>
<td>MEMS</td>
<td>Micro-electro-mechanical System</td>
</tr>
<tr>
<td>mR</td>
<td>Microresonator</td>
</tr>
<tr>
<td>NEAS</td>
<td>Noise Equivalent Absorption Sensitivity</td>
</tr>
<tr>
<td>NNEA</td>
<td>Normalized Noise Equivalent Absorption</td>
</tr>
<tr>
<td>OPO</td>
<td>Optical Parametric Oscillator</td>
</tr>
<tr>
<td>PPLN</td>
<td>Periodically Poled Lithium Niobate</td>
</tr>
<tr>
<td>QCL</td>
<td>Quantum Cascade Laser</td>
</tr>
<tr>
<td>SNR</td>
<td>Signal-to-noise Ratio</td>
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<tr>
<td>TF</td>
<td>Tuning Fork</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
</tr>
<tr>
<td>WMS</td>
<td>Wavelength Modulation Spectroscopy</td>
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</table>

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REFERENCES

PHOTOACoustic SPECTROSCOPY IN TRACE GAS MONITORING


64. S.T. Persijn, E. Santosia, F.J.M. Harren, ‘A Versatile Photoacoustic Spectrometer for Sensitive Trace-Gas
PHOTOACOUSTIC SPECTROSCOPY IN TRACE GAS MONITORING

Analysis in the Mid-Infrared Wavelength Region (5.1-8.0 and 2.8-4.1 μm), Appl. Phys. B, 75, 335–342 (2002).


76. LSE-Monitors, http://www.lsemontors.nl


