



**INNOVA**  
AirTech Instruments

# Photoacoustic Spectroscopy

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This booklet answers some of the basic questions about detecting gases using Photoacoustic Spectroscopy (PAS).

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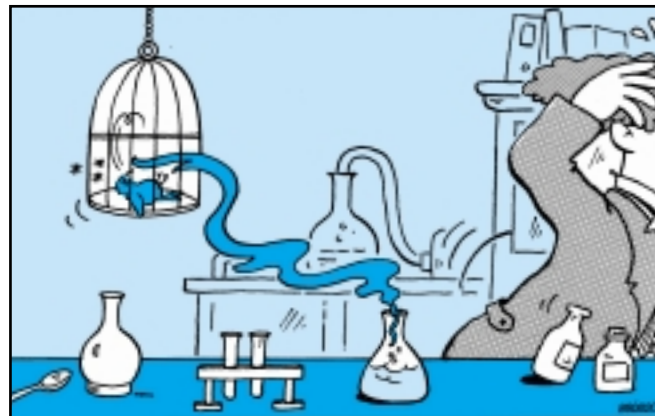
## Introduction

Industrialisation, along with concern for human safety and the environment, has stimulated the demand for sensitive and reliable methods of detecting trace amounts of toxic and polluting gases.

Early gas detectors were fairly primitive. The most popular was perhaps a canary in a cage: When the bird keeled over the workers got out! The canary has long since been superseded by a great variety of techniques, which can tell with relative ease which gas caused your bird to keel over and how much gas there was. These more up-to-date methods are based on a wide range of measuring principles such as spectroscopy, chromatography, chemical reactions and electrochemical detection.

Despite the large number of techniques available, it is not always an easy task to select the most suitable one. Infrared spectroscopy is always a popular choice. It is sensitive, selective, has a fast response time and a high immunity to interferences. A major advantage of spectroscopic methods for monitoring purposes is that no expendable materials are used and so maintenance costs and the amount of surveillance necessary are greatly reduced.

One form of spectroscopy, which offers particularly high sensitivity, is Photoacoustic Spectroscopy.



# Photoacoustic Spectroscopy

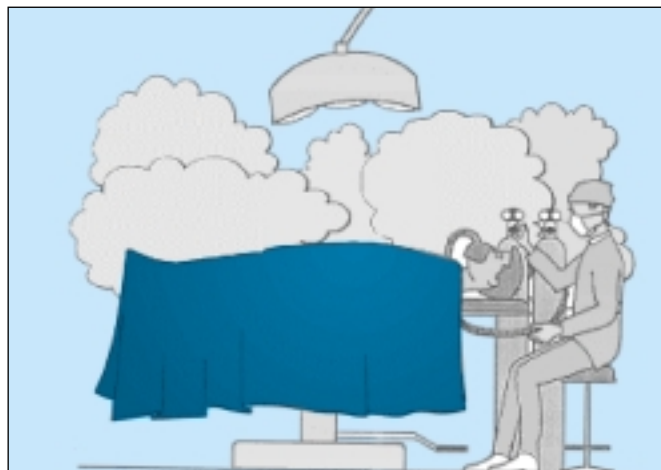
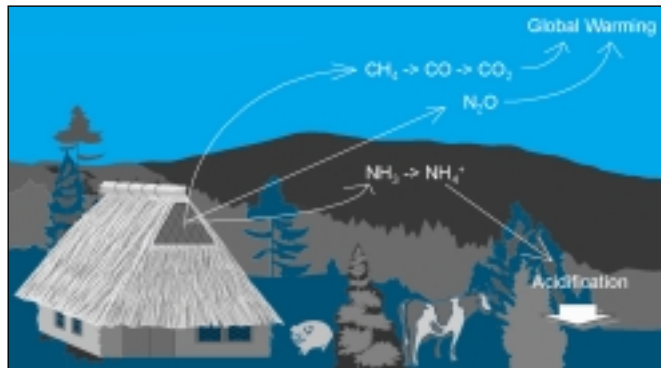
In recent times there has been a great revival of interest in Photoacoustic Spectroscopy (PAS) because it offers much greater sensitivity than conventional spectroscopic techniques. All spectroscopic methods yield quantitative and qualitative information by measuring the amount of light a substance absorbs; PAS simply measures this in a more sensitive way.

There is a tremendous need for high sensitivity in gas detectors. Present-day research establishments and industries often deal with highly toxic gases, which are hazardous at very low levels. Our daily lives generate an unpleasant array of polluting gases, some of which are dangerous with long term exposure to trace amounts. Because of its superior sensitivity to comparable techniques, PAS is of particular benefit when human safety is involved.

Gas detectors based on PAS find many applications, both outdoor and indoor. Typical examples are:

- Monitoring and identification of toxic and polluting gases in the atmosphere.
- Monitoring of organic compounds in production plants, laboratories and hospitals.
- Process control such as Fermentation Monitoring and Pure Gas Manufacturing.

Although PAS is a well-established technique, Innova AirTech Instruments are the first to apply it in dedicated commercially available gas monitors. This booklet is a general introduction to the topic, covering both the mechanisms of the procedure and the practical considerations. The first stage of the process, the absorption of infrared radiation, is common to all infrared spectroscopy techniques while the acoustical method of measuring the absorbed radiation is unique to PAS.



## The Early Days

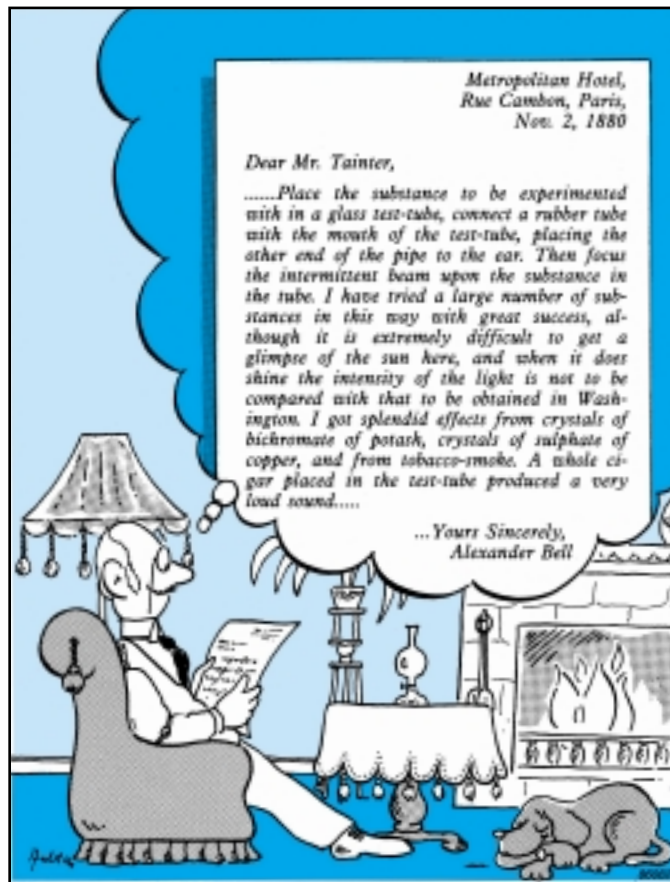
Although many people's response to Photoacoustic Spectroscopy is - "What? Never heard of it!" - it has, in fact, been around for quite some time now. The photoacoustic effect, which is the emission of sound by an enclosed sample on the absorption of chopped light, was first noted in the last century by the great all-round scientist, Alexander Bell, who accidentally discovered it during his investigations into the photophone.

He describes his early experiments, conducted while in France, in a letter to an American colleague\*. From them we can conclude that the French climate did not appeal to him and that he was most likely a cigar smoker.

Many other eminent scientists of the time, Tyndall and Röntgen among them, were extremely interested in this phenomenon. Unfortunately though, the only acoustic detectors then available were their ears, which made it rather difficult for them to quantify their results. Because of this limitation, interest in PAS waned.

Despite the invention of the condenser microphone in the 1930s, PAS remained a minority technique until the 1960s when interest in it was revived. Since then photoacoustics, or optoacoustics as it is sometimes called, has proved to be an extremely exciting field, with new applications and refinements being found regularly.

\* Contained in Bell, A.G. (1881)  
"Philos. Mag." 11(5)510



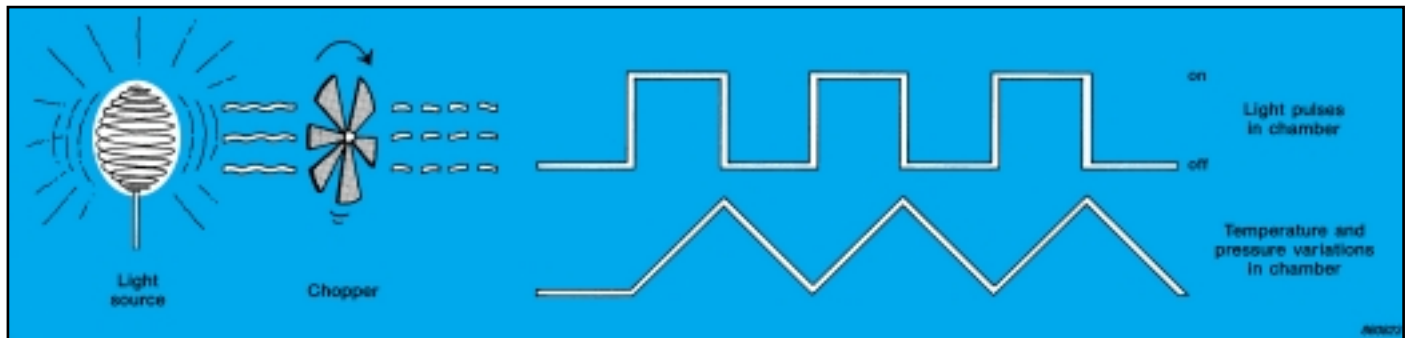
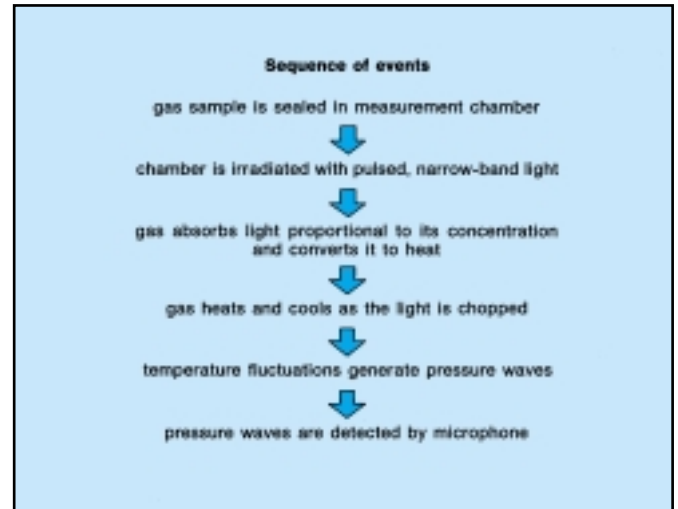
# The Photoacoustic Effect

The phenomenon known as the photoacoustic effect is the emission of sound by an enclosed sample on the absorption of chopped light.

When a particular gas is irradiated with light, it absorbs some of the incident light energy. The amount of energy it absorbs is proportional to its concentration. The absorbed light energy is immediately released as heat and this causes the pressure to rise. When the incident light is modulated at a given frequency, the pressure increase is periodic at the modulation frequency. Pressure waves, or sound waves as they are commonly known, are easily measured with a microphone. They are audible if their frequency is between 20 Hz and 20 kHz.

The intensity of the sound emitted depends on a number of factors: the nature and concentration of the substance and the intensity of the incident light.

The selectivity that can be achieved in spectroscopy is due to the fact that substances absorb light of specific wavelengths which are characteristic of that substance.



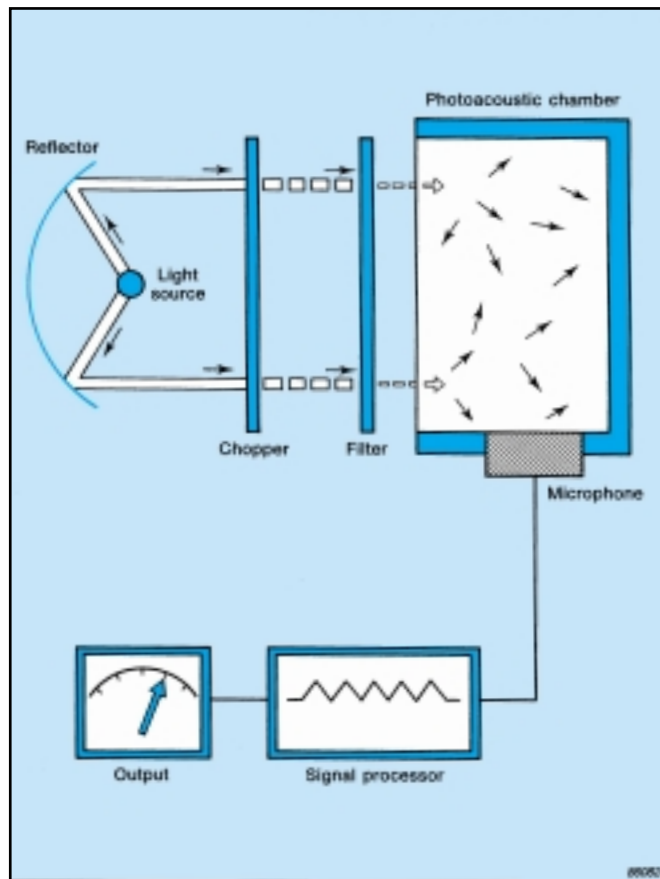
## A Typical Set-up

The essential components of a photoacoustic set-up are:

- A chamber to contain the gas sample
- A light source
- Some means of modulating the light (usually a chopper)
- A detector to measure the sound (usually a microphone)
- Some method of processing the signal (the level of sophistication of the signal analysis depends entirely on the requirements)

If the light source is incoherent (contains many wavelengths), an optical filter is used to resolve the radiation, enabling selective detection of a specific substance in a gas sample. Several optical filters can be mounted on a filter wheel to allow selective detection of different gases in one sample.

Photoacoustic instruments designed for automated sampling incorporate additional components such as a pump, air filters, etc. A full photoacoustic set-up is quite compact and can be accommodated in a portable instrument.





## The Light Source

The type of light source most suited to gas detection and analysis is one, which emits radiation in the infrared region of the electromagnetic spectrum, particularly between  $650$  and  $4,000\text{ cm}^{-1}$ . (A discussion of electromagnetic radiation and the units used is contained in the Appendix).

Sunlight is the most common infrared light source and is what Alexander Bell used in his pioneering experiments in photoacoustics. Although undoubtedly the cheapest source available it is not, as he himself commented, the most reliable!

An excellent and more dependable alternative to sunlight is an incandescent source. The simplest type is a wire filament heated to a high temperature. It has the major advantage of being stable, inexpensive and long lasting. The spectral output is continuous, with 70 - 80 % of it in the infrared region.

Narrow bandwidth radiation is required for spectroscopy and for this reason an incandescent lamp is used in conjunction with an optical system which selectively admits the desired wavelength band. Filters are used for fixed wavelength irradiation. For continuous tunability, diffraction gratings, prisms or interferometry can be used.





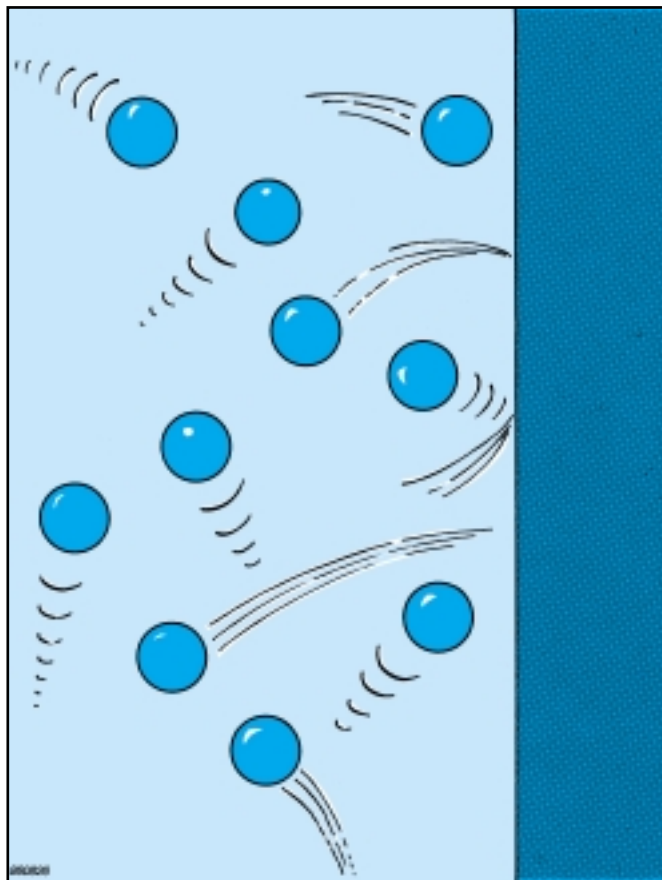
## The Nature of a Gas

To understand why infrared light, when shone on a gas, is absorbed at characteristic wavelengths and why sound is subsequently emitted, it is necessary to understand something of the nature and molecular structure of a gas. We will have a quick look at this in the next few sections.

Let us start at the basics. A gas is a collection of identical molecules, which are in continuous random motion. In fact, the name gas comes from the Greek word for chaos which describes exactly the way in which gas molecules move chaotically about, constantly colliding with one another and the walls of the containing vessel.

Gas molecules travel at amazingly high speeds and the temperature of a gas is proportional to the molecular speed. At  $20^{\circ}\text{C}$ , a small molecule, such as the Carbon dioxide molecule, whizzes around at  $407\text{ ms}^{-1}$  (920 m.p.h.). At  $40^{\circ}\text{C}$ , its speed goes up to  $421\text{ ms}^{-1}$ .

The constant bombardment of high-speed molecules against a container wall gives rise to a steady pressure (pressure is force per unit area). As the temperature increases, the molecules collide against the container walls at a greater speed and a higher pressure is recorded. For example, if Carbon dioxide is sealed in a container at atmospheric pressure at  $20^{\circ}\text{C}$  its molecules will exert a pressure of  $1.013 \times 10^5\text{ Pa}^*$  on the walls of the container. By increasing the temperature of the gas in the sealed container to  $40^{\circ}\text{C}$  the pressure of the gas molecules will increase to about  $1.08 \times 10^5\text{ Pa}$ .



\*  $1\text{ Pa} = 1\text{ N/m}^2$

$1.013 \times 10^5\text{ Pa} = 1\text{ atm} = 760\text{ mmHg}$

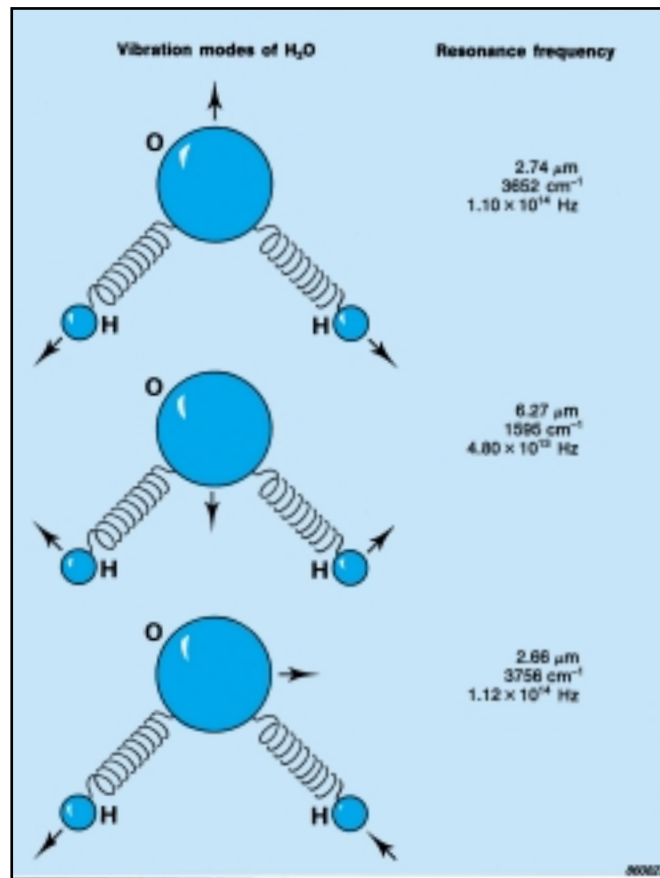
## Molecular Vibrations

Individual gas molecules are built up of a number of atoms bonded to one another. Take for example the Ammonia molecule,  $\text{NH}_3$  that is made up of one Nitrogen and three Hydrogen atoms. Ammonia gas consists of a large number of these molecules moving about in space. To envisage the numbers involved, consider that a one litre vessel filled with Ammonia would contain approximately  $3 \times 10^{22}$  individual molecules.

The atoms in a molecule are also in constant movement but because their movement is constrained by the interatomic bonds, the atoms vibrate to and from in fixed vibration modes. These vibrations are at a certain frequency, called the resonance frequency, which is determined by the mass of the atoms and the strength of the chemical bonds.

Because of the smallness of scale, the resonance frequency of molecules is in the order of  $10^{13}$  Hz - that is 10,000,000,000,000 vibrations a second! Compare this to a weight vibrating on a spring. A 1-kg weight on a medium strength spring would vibrate at about 1 Hz. (The resonance frequency depends on the mass and on the stiffness of the spring).

Each molecule has a number of vibration modes. The bigger the molecule, the more modes it possesses. A molecule with four atoms has six vibration modes whereas one with ten atoms has twenty-four. As mentioned above, the resonance frequencies of these modes are determined by the molecular structure and are always the same for a given molecule. The three vibration modes and corresponding resonance frequencies of the water molecule,  $\text{H}_2\text{O}$ , are given here.

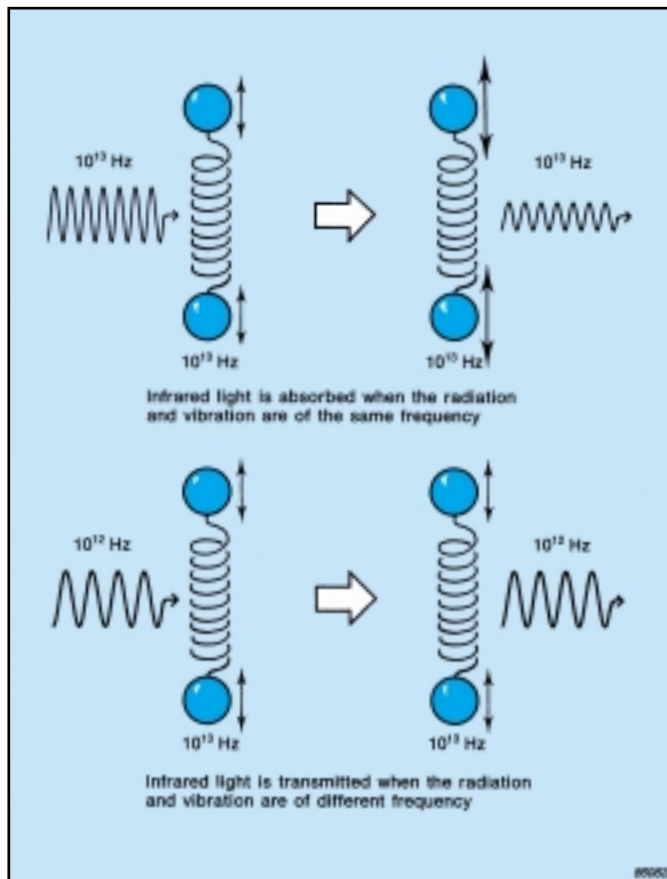


## Absorption of Infrared Light

The frequency of infrared radiation is of the same order of magnitude as molecular vibrations; approximately  $10^{13}$  Hz. Infrared radiation can interact with a molecule and transfer energy to it, and only if, the frequency of the radiation is exactly the same as the frequency of a vibration within the molecule. When the molecule absorbs this radiation it vibrates with greater amplitude (but at the original frequency). References to the frequency of the light should not be confused with either the modulation frequency of the chopper or the frequency of the sound signal produced (which is at the modulation frequency).

In other words, when light of a broad spectral content is passed through a gas, some of the frequencies are absorbed while the rest are transmitted without being absorbed. Those frequencies, which are absorbed, correspond to the natural frequencies of the vibration modes of the gas molecules or to a harmonic of these vibrations. Similarly, when monochromatic light is passed through a gas, it will only be absorbed if the frequency of the monochromatic light is the same as a vibrational frequency of the gas molecule. The amount of light absorbed is directly proportional to the concentration of the gas.

An electric dipole moment is created when there is a difference between the density of charges on the various atoms in a molecule. Only those gases, which, as a result of their vibrational or rotational motion, undergo a net change in electric dipole moment, can interact with infrared light (an electromagnetic wave). Single-atom gases/vapours (e.g. Helium He and Mercury Hg) and homonuclear gases (e.g. Oxygen  $O_2$  and Chlorine  $Cl_2$ ) therefore cannot absorb infrared light.



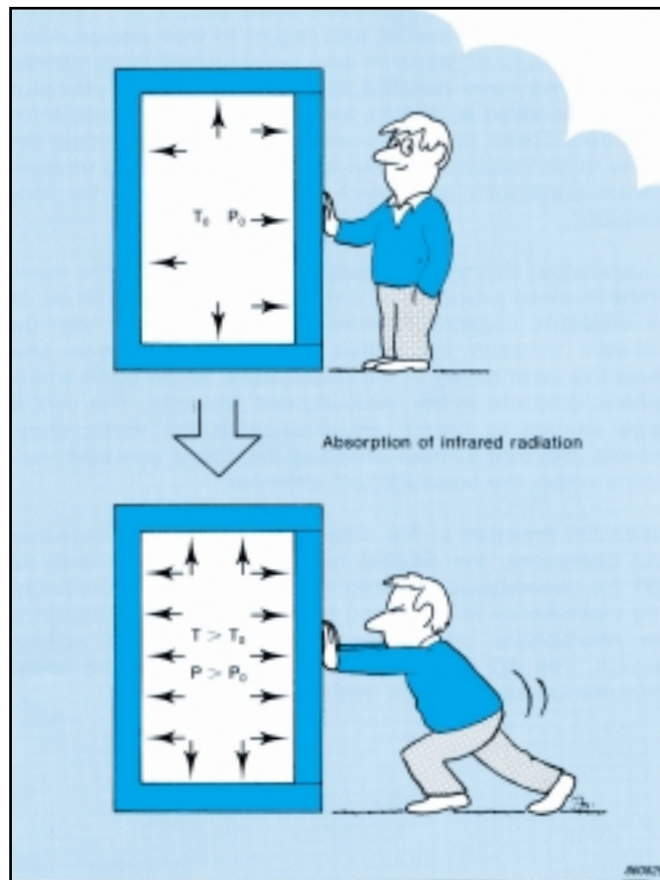
## Release of Absorbed Energy

When a molecule absorbs infrared radiation, the molecule gains energy and vibrates more vigorously. This increased activity is short-lived, however, and the excited molecule very quickly transfers its extra energy to other molecules in the vicinity by colliding with them and causing them to travel more quickly.

Increased molecular speeds means that the temperature in the measurement chamber increases and, when the chamber is sealed, the pressure also increases.

The amount of light absorbed can be measured by measuring either the heat energy released or the associated pressure increase. Both parameters are proportional to the concentration of the absorbing species. Because calorimetric detectors have slow response times and are insufficiently sensitive, the pressure increase is the preferred measurement parameter.

A microphone is an excellent detector of fluctuating pressure, offering high sensitivity, stability and a wide dynamic range. Because a microphone detects fluctuating rather than steady pressure changes, the incident light beam of a photoacoustic set-up is modulated in order to give varying pressure levels in the measurement chamber.

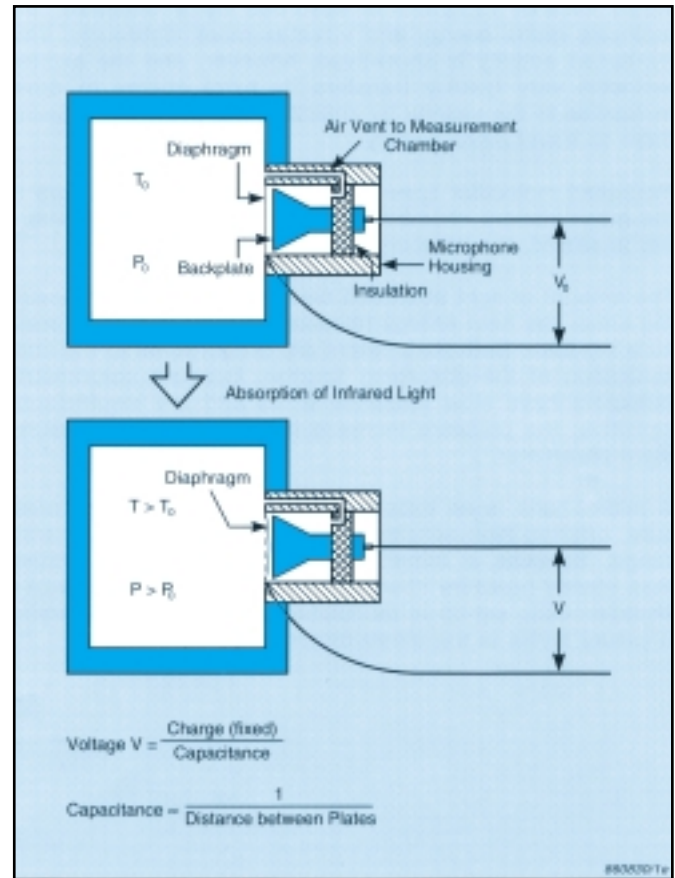


## How a Microphone Works

When it comes to microphones, many people are unaware of the high state of the art with regard to their design. More than fifty years of research and development in condenser microphones have resulted in a sensitive, high precision transducer, which is reliable, stable and extremely well characterised. These features combine to make it an ideal detector in an instrument which is exposed to severe environmental conditions and which is left unattended for long periods.

A condenser microphone consists of a thin metallic membrane in close proximity to a rigid backplate. This forms an air dielectric capacitor the capacitance of which varies with the distance between the plates. A small equalisation tube vents the inner cavity of the microphone to the static atmospheric pressure in the measurement chamber. The vent is large enough to permit equalisation of the static atmospheric pressure without affecting the sound pressure variations within the measurement chamber.

When the pressure in the measurement chamber increases and decreases, the flexible membrane moves in and out and the capacitance between the plates varies accordingly. The capacitance is measured by applying a fixed charge to the microphone and measuring the associated voltage change. The AC voltage is an exact replica of the sound pressure variations in the measuring chamber.



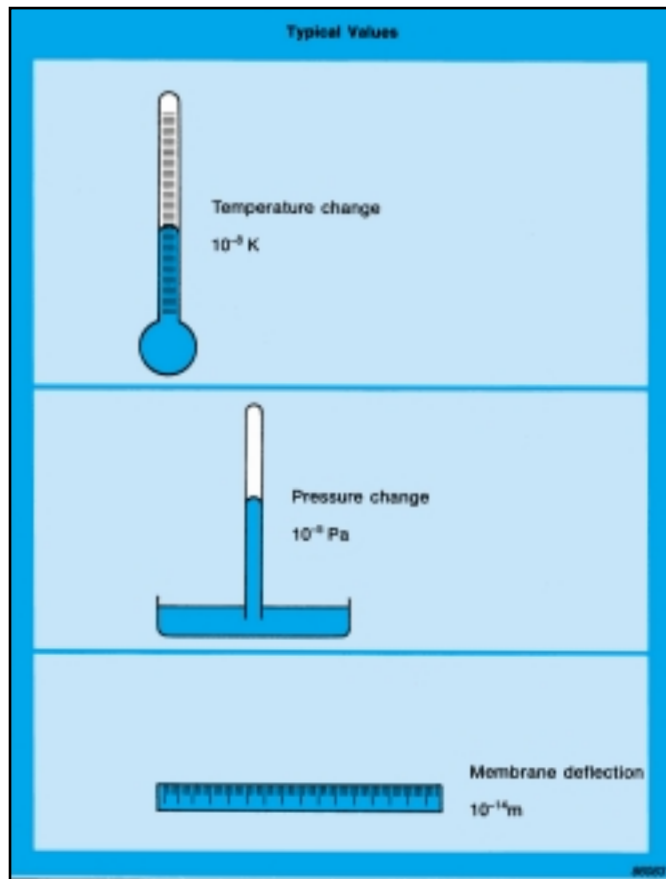
## Typical Dimensions

When trace amounts of an absorbing gas are present in the photoacoustic measurement chamber, the resultant temperature and pressure changes and membrane deflections are extremely small.

For an absorbing gas which is present at concentration close to its lower limit of detection (parts-per-billion ( $10^6$ )), the temperature increase in the measuring chamber is typically  $10^{-8}$  K. The corresponding pressure increase in the chamber is below the threshold of hearing (which is  $20 \mu\text{Pa}$ ) and is approximately  $10^{-5}$  Pa. This deflects the membrane of a  $1/2''$  microphone by a mere  $10^{-14}$  m - a distance only slightly greater than the diameter of an electron:  $10^{-15}$  m. To express the scale of the deflection another way, a microphone membrane the size of the Earth would deflect only 0,1 mm under the same measurement conditions!

Despite these diminutive values, a microphone with a sensitivity of about  $50 \text{ mV/Pa}$  allows trace concentrations to be measured with relative ease.

The specifications of a condenser microphone are remarkable. It typically offers a dynamic range of over seven orders of magnitude and a response time in the order of  $10 \mu\text{sec}$ . A microphone's high stability is illustrated by the fact that at room temperature its sensitivity will theoretically change by less than 1.1 % in 250 years. Microphones are the transducers used to measure signals in instruments based on photoacoustic measurement technology, and therefore these instruments are also very stable. Most instruments only require calibration checks once every 3 months.



## An Infrared Spectrum

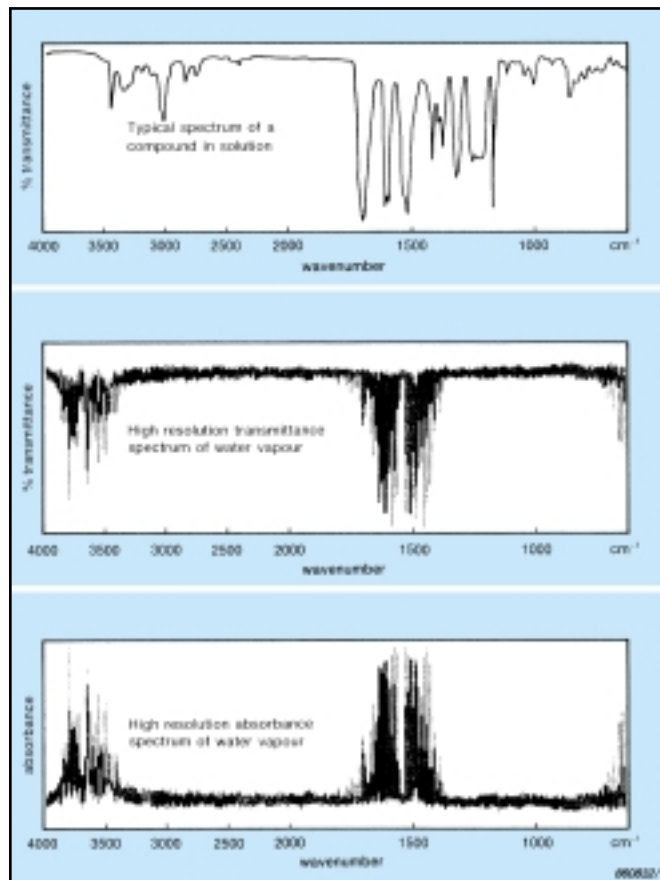
If a gas is irradiated with infrared light scanned from say 2.5  $\mu\text{m}$  to 15  $\mu\text{m}$ , some of the light will be absorbed and some transmitted. By measuring the amount of light absorbed (or transmitted) at each wavelength an infrared spectrum can be constructed. The general name for an instrument, which gives a spectrum, is a *spectrophotometer*.

There are two methods of presenting the amount of light absorbed, either in terms of % *transmittance* or in terms of *absorbance*. The relationship between *absorbance* (A) and *transmittance* (T) of a gas at a particular wavelength is:

$$A = \log \left\{ \frac{1}{T} \right\}$$

In traditional infrared transmission spectroscopy, % transmittance is measured directly and substituted in the above equation to obtain absorbance. The disadvantage with this method is that any error in the measurement of T introduces an even greater error in the calculated absorption. This problem is avoided by measuring absorption directly using the photoacoustic method. The photoacoustic method is therefore more accurate and is preferred for qualitative analysis because the measured absorption is directly proportional to the gas concentration.

Three typical spectra are presented here. The frequency of each absorption band corresponds to the natural frequency of a vibration mode of the molecule or a harmonic of a vibration. Liquids and solids have broad absorption bands, which are resolved into discrete lines in gaseous samples.





## Qualitative Analysis

Each substance has a unique infrared spectrum. The spectra of almost all known compounds are compiled in various reference volumes and the identity of a substance can be confirmed by comparison of its spectrum with these standard spectra. This kind of investigation can now be carried out far more rapidly than was previously the case because of current advances in computer storage and retrieval.

Well-resolved spectra yield detailed structural information such as bond lengths. PAS has proved very useful in investigating de-excitation processes in gases and other kinetic studies.

## Quantitative Analysis

The strength of the absorption is proportional to the amount of absorbing species present. By calibrating with a standard sample of known concentration, the concentration can be determined.

When a large variety of samples are being regularly analysed, a spectrophotometer is normally used. For regular quantitative analysis of a small number of known gases, it is usually sufficient to irradiate the sample at the wavelengths at which the gases of interest absorb strongly. This simpler instrument, which does not output a spectrum, is generally referred to as a *filter* or *fixed-wavelength photometer*.



## Detection of Specific Gases

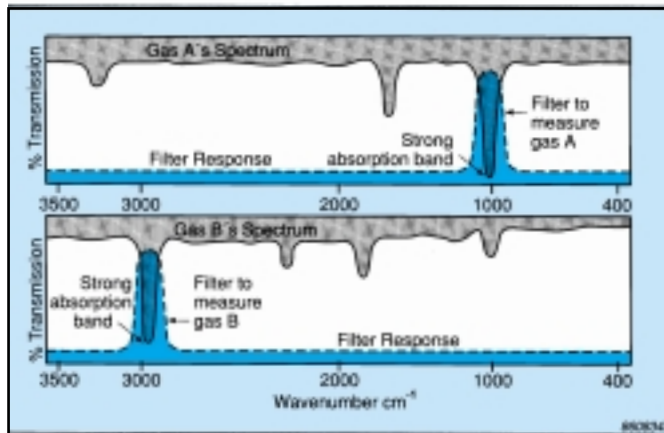
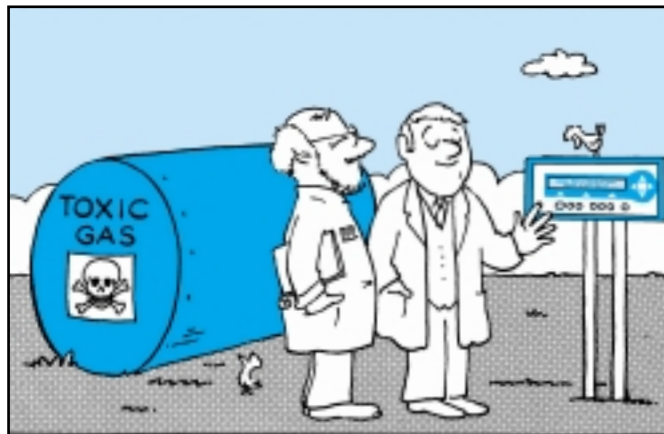
Consider the case of the manager of a chemical storage plant who wishes to monitor the concentration in air of a single toxic gas. In this application, a fixed-wavelength gas detector, which responds only to that specific gas, is the obvious choice.

To select the irradiation wavelength, the infrared spectrum of the gas of interest is studied and the strong absorption bands noted. The stronger the absorption, the lower the limit of detection for the gas. The spectra of all possible contaminants are then carefully inspected for absorption at those wavelengths. A wavelength can usually be found at which the gas of interest absorbs strongly but interferences do not.

Similarly, if you wish to detect a number of gases in a single air sample, it is possible to irradiate the sample at a number of fixed wavelengths, chosen as described above.

Almost all existing gases can be detected by this method. The detection limit depends on the particular gas; the selectivity (that is, its immunity to interfering species) depends on the measurement environment.

If interference between two gases is unavoidable, a monitor, which is able to detect several gases in a single sample, can reduce, and sometimes overcome, the problem by *cross-compensating* for the presence of the interfering species. The concentration of the gas of interest (gas A) is measured; the concentration of the interfering gas (gas B) is also measured, but at a different, yet still strongly absorbed wavelength. From these measurements it is possible to calculate the gas B's influence on gas A's measurement and thus find gas A's true concentration.



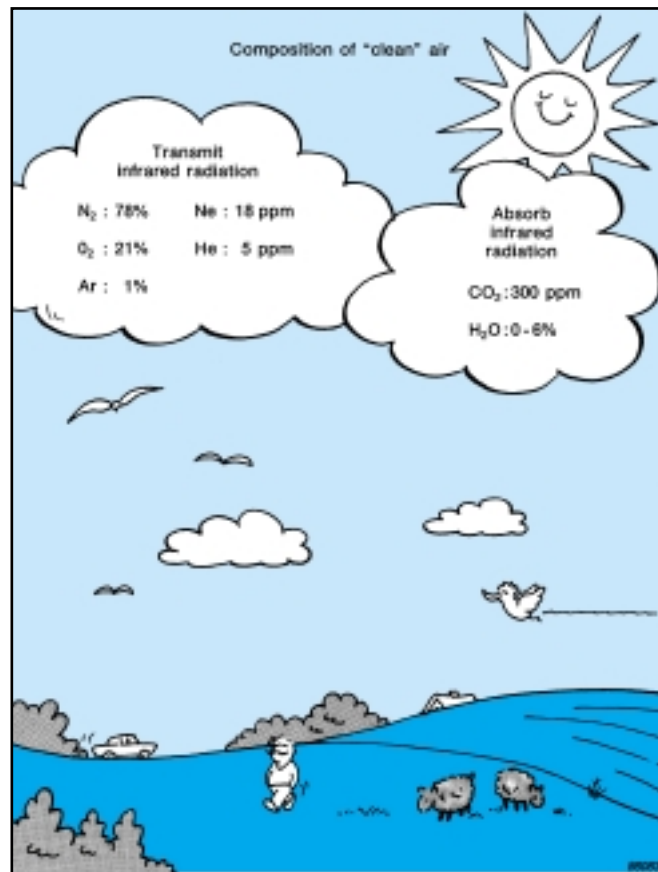
## Interfering Species

Toxic and polluting gases are normally found as trace components in atmospheric air. The various gases which are found in normal atmospheric air are therefore potential interferents when detecting toxic and polluting gases. Fortunately however, the main constituents of air do not absorb infrared radiation at all, as is illustrated by the simple fact that we get heat from the sun. Only two minor constituents, water and Carbon dioxide, absorb infrared light and these are present in low concentrations.

Immunity to interfering species is perhaps the most important consideration in any gas detection method. Because gases absorb infrared light over a narrow spectral range and only at characteristic wavelengths, instruments based on infrared absorption spectroscopy offer greater selectivity than most other techniques.

It sometimes happens that the most likely interference is of very similar structure to the gas of interest. Consequently, their spectra are also very similar and there is considerable overlap of absorption bands. In such cases, high selectivity can still be obtained by irradiating at two wavelengths at which the gases have different ratios of absorption.

This is how to cope with any interference caused by the presence of atmospheric water vapour and Carbon dioxide. Air samples are irradiated by light at two different wavelengths, one, which corresponds to a strong absorption band of water vapour and the other of Carbon dioxide. From these measurements it is possible to compensate each measurement for interference from these two gases/vapours.

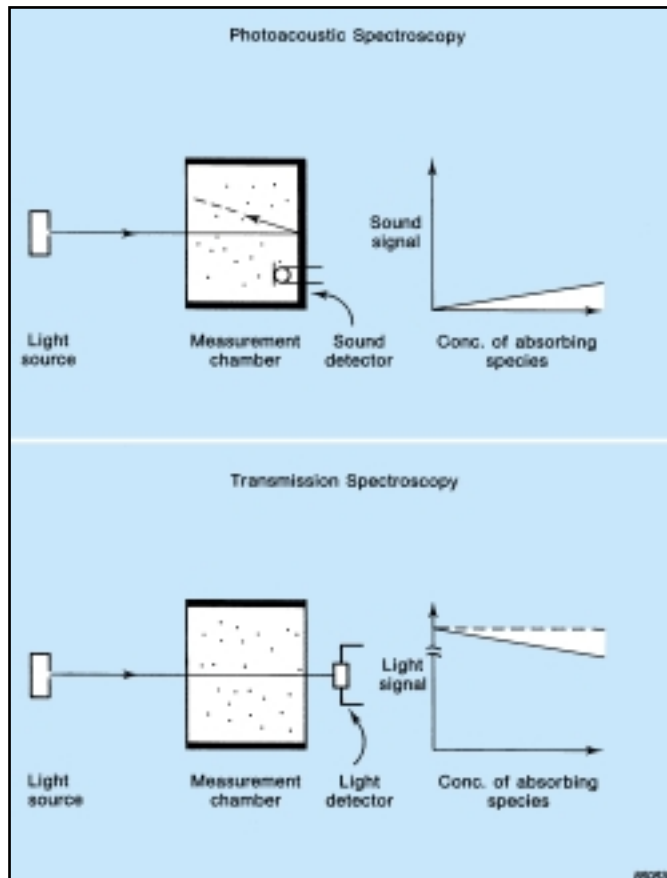


## PAS and Transmission Spectroscopy Compared

As we have discussed in the preceding pages, those instruments using the photoacoustic detection method and those using conventional transmission spectroscopy are both based on absorption of infrared light. The fundamental difference between the two techniques is the detection method. In PAS the amount of light energy absorbed is measured directly by measuring the sound energy emitted when gas molecules absorb the light. In the absence of a light-absorbing gas, no signal is obtained.

In conventional transmission spectroscopy light is passed through the measurement chamber and a light detector measures the amount of light transmitted through the cell. It is easy to see that, in the case where the absorbing gas is present in very low concentration or the gas does not absorb the light strongly, almost as much light is transmitted in the presence of the sample as in its absence. As the difference between two almost equal signals is being measured, the signal to noise ratio is poorer with transmission spectroscopy than with PAS and therefore it is a less sensitive technique.

As mentioned earlier, PAS is a more accurate technique as it measures absorption directly. The PAS method has additional advantages over conventional transmission spectroscopy. It uses a very stable transducer (microphone) so calibration is seldom required more than 4 times a year (contra daily/weekly). The linear response of the microphone enables measurement of gas concentrations over a wide dynamic range (typically 4 - 5 orders of magnitude) without having to change the range setting or to recalibrate. It uses a small volume of gas ( $\sim 3 \text{ cm}^3$ ) in the measurement cell (contra  $\sim 3 - 4,000 \text{ cm}^3$ ) - thus reducing the time between measurements (i.e. response time is fast).



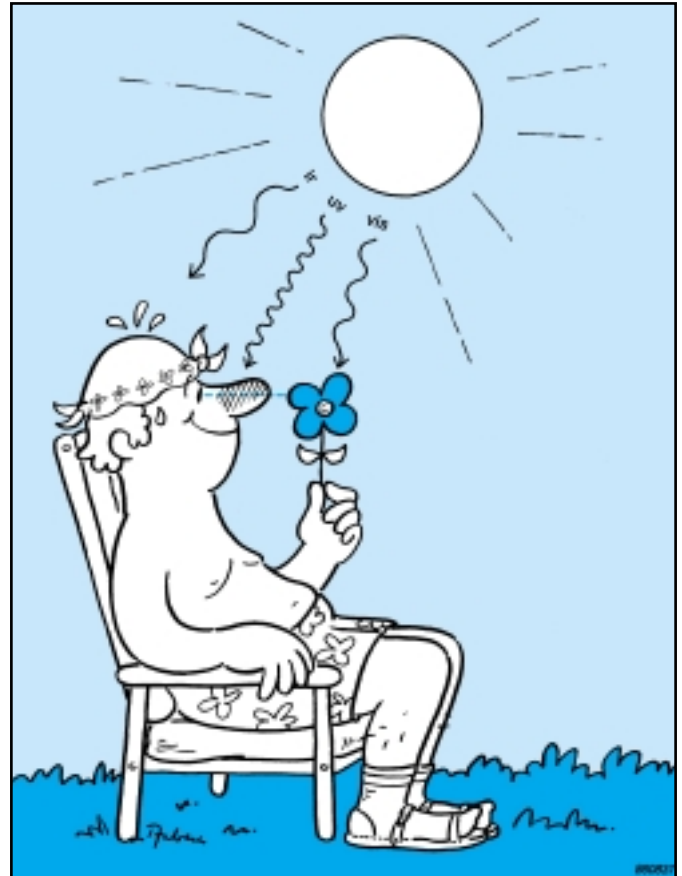
## An Everyday Experience

The bandying about of terms such as "absorption", "emission", "infrared radiation", etc. may seem a little obscure to those new to the field. It is worthwhile to realise that absorption of electromagnetic radiation and its subsequent emission are everyday events, and not merely confined to the laboratory and instruments called spectrophotometers. Evidence of these phenomena is all around us.

The reason an object is coloured red, for example, is because it absorbs the blue light and reflects the red light.

Your skin warms up in the sun because the molecules in your body absorb the infrared radiation and vibrate more energetically.

The sunburn you get from over-exposure is due to the absorption of ultraviolet rays into the skin. To help prevent this, many sun-barrier creams are based on chemicals, which are strong absorbers of ultraviolet radiation.



## Gas Monitoring – Special Considerations

Additional demands are made on a gas detector when it is installed as a long-term monitor. Factors such as reliability, stability, and ease of operation are of major importance. The general features of a photoacoustic detector in this regard are discussed here.

## Maintenance

The majority of gas detection methods have now been automated to a greater or lesser extent. However, the length of time a monitor can be left unattended depends on the need to replenish any materials which are used up, the stability of the instrument (hence the interval between calibrations) and the reliability of the individual components.

Monitors based on spectroscopy do not consume any materials, and therefore offer a great advantage over methods which do. PAS brings the additional benefit of using microphones as detectors. The stability and reliability of modern, high-precision microphones means that calibration of a PAS monitor is only necessary at infrequent intervals, typically three months, resulting in low maintenance requirements. Compared to monitoring systems currently available, which require weekly and even daily attention; a monitor based on PAS is extremely cost-effective.



## Resistance to the Environment

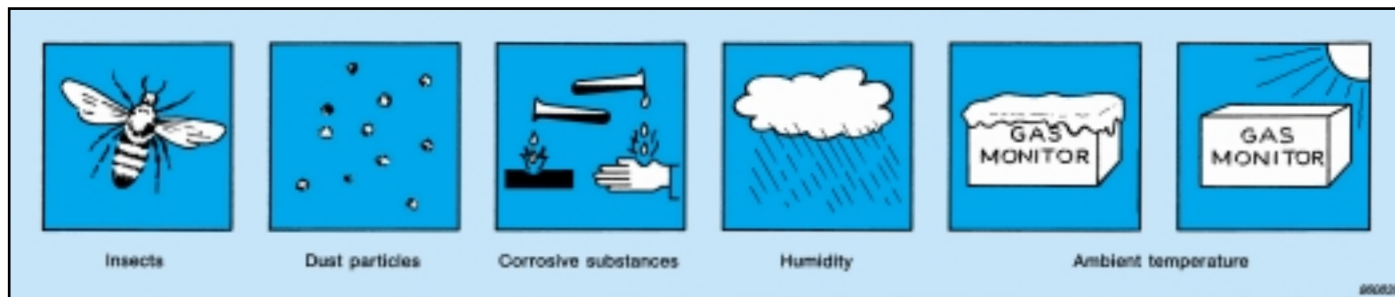
Because gas monitors are often located in harsh indoor and outdoor environments, resistance to the elements is of crucial importance.

Some of the conditions a monitor must withstand are illustrated below. Flying objects and dust particles can be removed from the air samples by filters at the air inlet. All components must be designed to have a high corrosion resistance. Extremes of ambient conditions should not affect the accuracy of the result. As the reliability of the instrument as a whole depends on the reliability of each individual part, every component must be designed to last, with particular regard to the extremely taxing conditions found in industrial applications.

## Dynamic Range and Accuracy

Due to the very linear response of a precision microphone, the response of a photoacoustic cell is linear over a wide dynamic range - typically four to five orders of magnitude (e.g. from 1 ppm to 10,000 or 100,000 ppm). This allows the same instrument to be used for monitoring both the trace amounts of pollutants, which are generally found in ambient air, and the high concentrations, which are found at the source.

It is essential that toxic gas concentrations are measured accurately. The low range-drift of a PAS monitor enables accurate measurements to be performed over long periods of time. Typical reproducibility is 1 % of the measured value with a range-drift of less than 2.5 % of the measured value in three months.





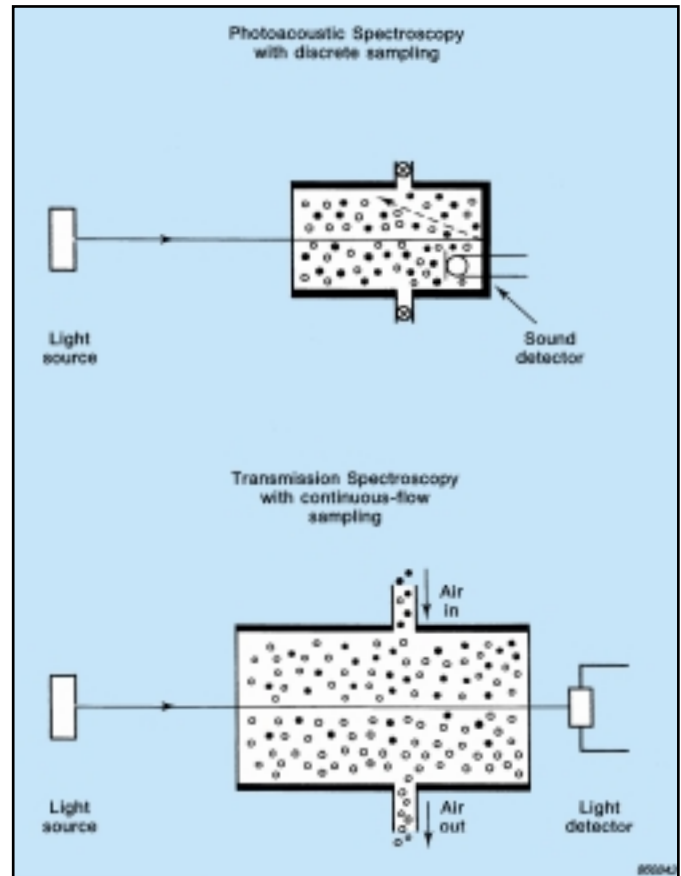
## Response Time

In order to give adequate warning, it is important that a gas detector, which is monitoring highly toxic gases, responds immediately when high concentrations are present.

In contrast to many other monitoring techniques, the measuring chamber of a photoacoustic monitor is sealed. Hence, the air must be analysed as discrete samples rather than continuously. Nonetheless, this does not adversely affect the response time because small cell volumes, typically  $3\text{ cm}^3$  can be used due to the high sensitivity available. Small discrete samples can be taken frequently and the true concentration of the ambient air measured.

Compare this to a typical transmission spectrometer, which requires large cell volumes of 3 - 4 litres to reach the necessary sensitivity. Although sampling is continuous, the incoming air mixes with the earlier air and so damps the response. On balance, the response time from both methods is comparable.

Another aspect which affects the response of a detector is the ease with which it can be purged. Many non-spectroscopic instruments have a long recovery time after a high concentration is detected - sometimes as much as one hour. The time taken to purge the cell and take a new measurement is typically less than 1 minute for a PAS based instrument.



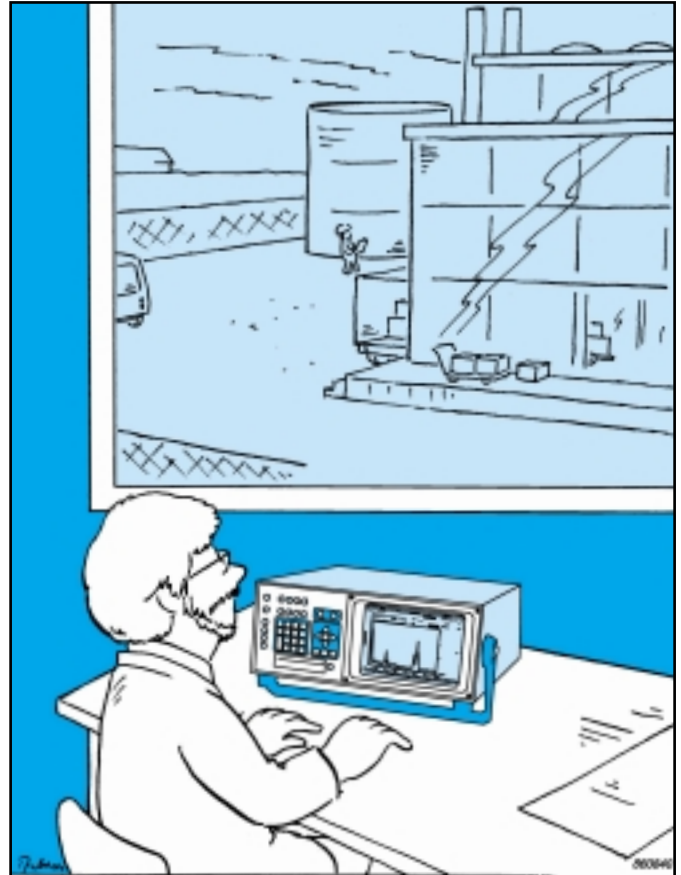
## Operation and Control

For continuous, long-term monitoring of gases it is essential that the monitors can operate automatically and without constant attention. Otherwise a disproportionate amount of manpower has to be used to supervise the monitoring system. In the case of highly toxic gases, remote control avoids exposing personnel to large doses.

Monitoring systems can also enhance the production process by giving valuable gas concentration parameters to the process engineer. Another critical parameter for continuous monitoring is the need for frequent calibration known from most measurement techniques. The distinct advantage of PAS in this application is the extreme stability of the microphones minimizing the need for calibrations.

INNOVA develops and manufactures systems that can monitor multiple points from a central location, including both continuous and discrete sampling systems. The systems can be connected to either PC's or process computers for further data processing or for activation of process controllers or operation alarms.

In order to protect the system from environmental hazards, such as condensation or dust, the system can be equipped with the necessary preconditioning.



# Implementation of Photoacoustic Spectroscopy

## 1. Discrete Sampling – Non-dispersive PAS

The non-dispersive (filter-based) PAS detector consists of very much the same components as the original setup used by Alexander Bell - an infrared light source, a chopper wheel and a measurement cell. Further, optical filters have been added to improve selectivity, as has a pump to bring the sample into the measurement cell.

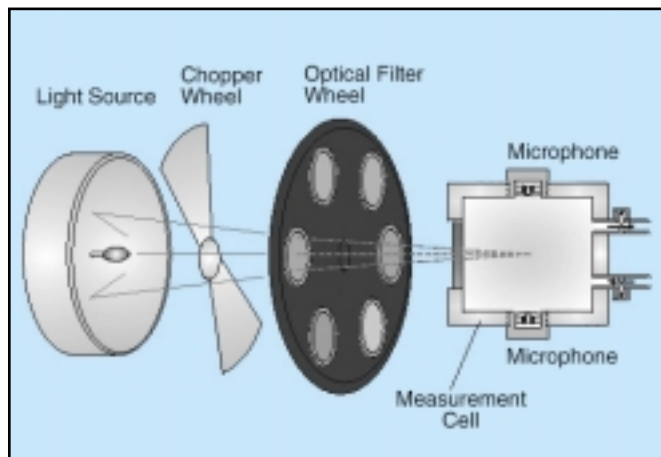
The infrared light source is placed in a parabolic mirror in order to concentrate and focus the IR-light inside the measurement cell. The chopper wheel, rotating with a well-defined frequency, will modulate the light, generating light-pulses which enter the measurement cell. The optical filter will ensure that only light at the selected wavelength enters the measurement cell.

The instrument works in a semi-continuous way. First, the pump purges the sample lines and the measurement cell in order to flush out the old sample and bring in the new one. The valves to and from the measurement cell are then closed and measurement starts: the IR-source is turned on, the chopper wheel starts rotating and the microphones pick up the photoacoustic signal. The optical filter wheel positions each of the optical filters in the light path, one after the other, until all filters have been measured. Finally the instrument calculates the concentration of each gas, the results are displayed and the whole procedure starts all over again.

One optical filter for the measurement of water vapour is installed in the filter wheel as standard. This way, the water vapour is measured in each sample, enabling the instrument to subtract the absorption signal coming from water vapour from the measured signal for a gas of interest, giving a more correct measurement. In a similar way, by measuring the same air sample with more optical filters, one filter

selected for each gas in the sample, the interference from one gas on another can be compensated for.

The entire measurement system is very compact (volume of the measurement cell is 3 cm<sup>3</sup>) and with a very low internal volume in the tubing and pump. Besides making the instrument very compact, it allows accurate measurements to be performed on even very small sample volumes. This, together with the outstanding stability of the PAS detector and the interference compensations, is the biggest advantage of the system.



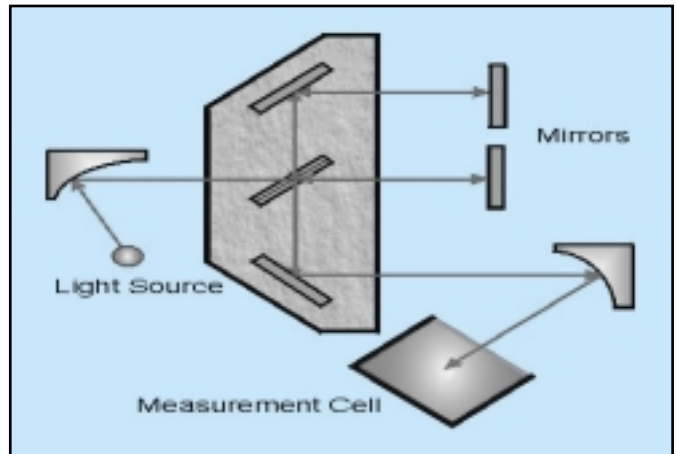
## 2. Discrete Sampling – FTIR/PAS

For analysing unknown gas samples in order to identify the components and to quantify them, the Fourier Transform IR-analyser (FTIR) has proven a powerful tool, especially in laboratories. Combining the FTIR technique with the PAS detector, the small, but very rugged and stable detector opens up new dimensions in FTIR by making it possible to make a portable FTIR analyser.

Basically a FTIR analyser is based on the same principles as a non-dispersive IR-monitor. But the chopper wheel and the optical filters have been substituted by a so-called Michelson interferometer. The interferometer consists of some mirrors and a beam-splitter. By splitting the IR-light into two beams: one which is reflected by a fixed mirror and one which is reflected by a moving mirror, and then combining the two beams again in the measurement cell, the combined beam is now modulated with a different modulation frequency for each wavelength of the light. This way the entire IR-range is "scanned" and the absorption at each wavelength is then measured

in the PAS detector. In other words it corresponds to measuring the gas sample with an infinite number of optical filters.

This way the entire IR-spectrum of the gas sample is obtained and on this basis it is possible to not only identify the various components of the sample but also measure the concentration of each component.



### 3. Continuous Flow – PAS

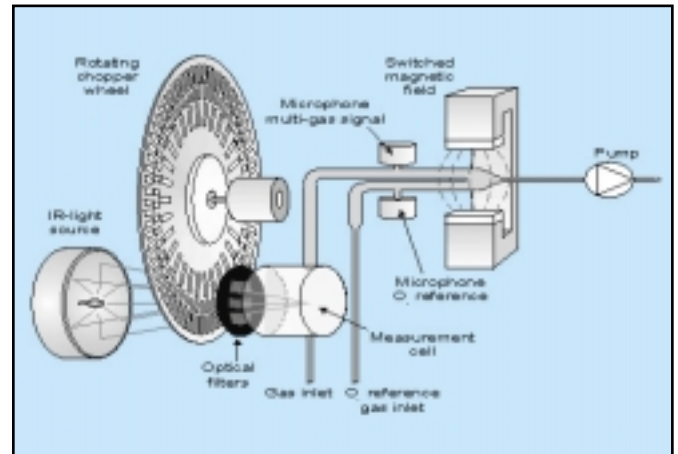
The PAS detector can also be used in a continuous flow system. By eliminating the inlet and outlet valves to the measurement cell and pumping the sample through the cell at a constant, well-controlled rate of flow, the continuous flow PAS system can perform real-time monitoring.

In this system the optical filters are combined to form the optical window through which the IR-light enters the cell. Passing the chopper wheel modulates the light, but this chopper wheel is perforated in different distances from the centre. When rotating the chopper wheel at constant velocity, three different modulation frequencies are obtained - corresponding to the three optical filters. A microphone picks up the photoacoustic signal downstream.

Due to the constant flow through the measurement cell the response time is extremely short. However, the constant flow creates turbulence in the cell, which the microphone detects as noise. Therefore the detection limit in a continuous flow system is higher than in a discrete sampling system.

As a special feature the PAS detector can be combined with a Magneto Acoustic detector (MA) for the measurement of Oxygen ( $O_2$ ). Oxygen does not absorb IR-light but it is paramagnetic. This means that if a switched magnetic field is applied to the gas stream, Oxygen will vibrate and the microphone will pick up the vibrations. By comparing the Oxygen measurement with a reference gas

(normally ambient air where  $O_2$  is constantly 20.95 % vol.), the MA detector can measure with an accuracy which can normally only be achieved with far more expensive Mass Spectrometers. As an example, this is particularly useful in Fermentation Monitoring where metabolic Oxygen consumption is an important indicator of the microbial activity.



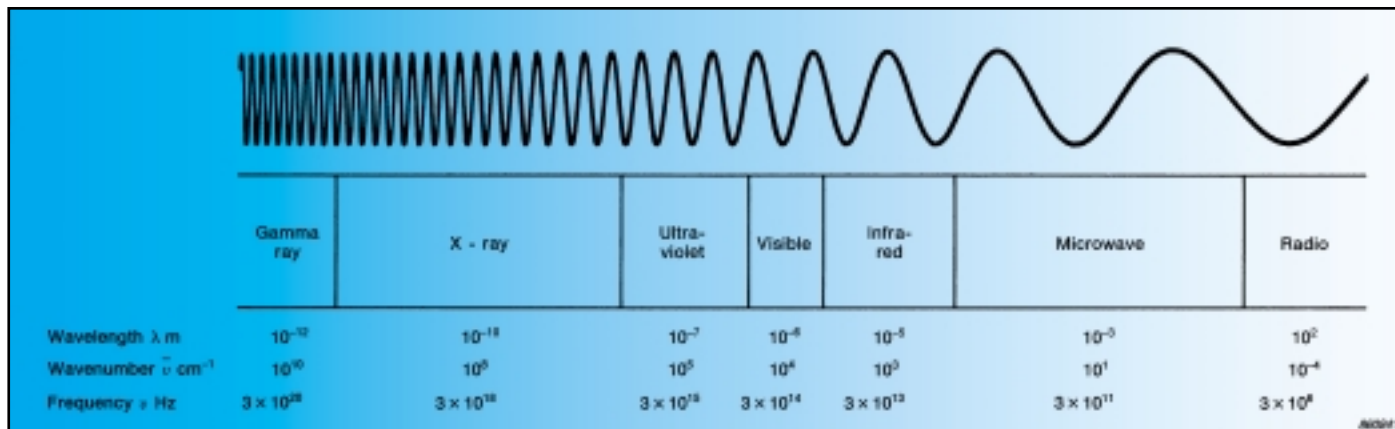
# Appendix

## Electromagnetic Radiation

Visible light, infrared radiation, radio waves and X-rays are all examples of electromagnetic radiation. The electromagnetic spectrum arranges radiation in order of magnitude and divides it into convenient regions, with lowenergy radio waves at one end and high-energy gamma waves at the other.

Materials absorb electromagnetic radiation in various regions and spectroscopy is the measurement of this absorption. Certain regions are of greater interest in science, particularly the microwave, infrared, ultraviolet/visible and X-ray regions. Each region is best suited to certain applications.

The infrared region is most useful for the quantitative and qualitative analysis of gases, the reason being that absorption here is highly selective and over a narrow spectral region. Its uniqueness means that the region from  $900\text{ cm}^{-1}$  to  $1,400\text{ cm}^{-1}$  is commonly referred to as the "fingerprint region".



## Units of Radiation

Three interrelated units are commonly used when describing electromagnetic waves: the frequency,  $\nu$  (Hz), the wavelength,  $\lambda$  (m), and the wave number,  $\bar{\nu}$  ( $\text{cm}^{-1}$ ).

Of these, chemists working within the field of infrared analysis most commonly use the wave number, largely because it gives more manageable numbers. As the mechanism of the interaction of infrared light with the molecule is easier to understand in terms of frequency, this unit is widely used in this text. The third unit commonly used, that of wavelength, is perhaps the most widely used descriptor over the entire electromagnetic spectrum and that is perhaps the unit people are most familiar with.

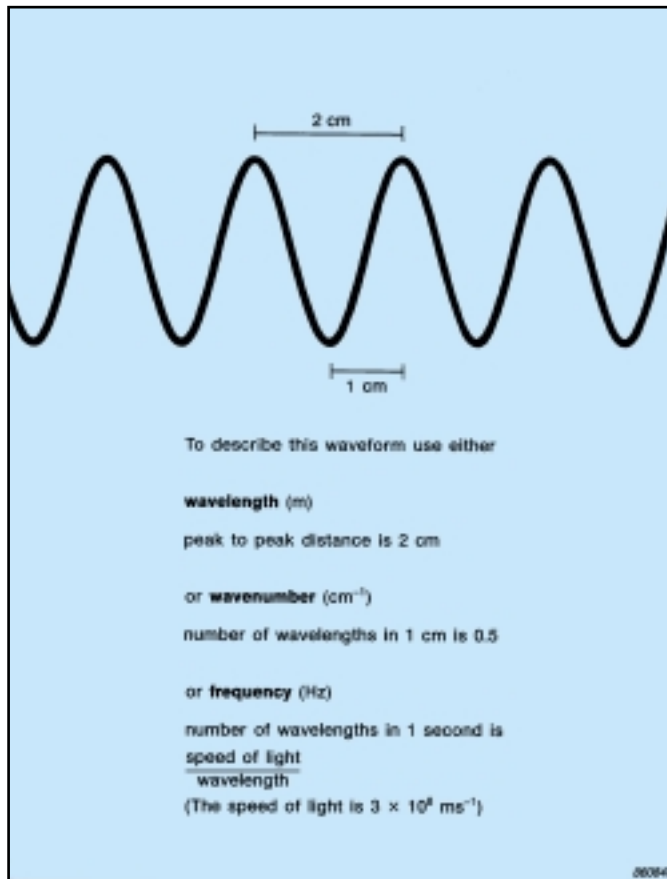
## Units of Gas Concentration

The two most commonly used units for describing the concentration of gases are  $\text{mg/m}^3$  and parts-per-million (ppm) by volume. Use the following equation to interchange from  $\text{mg/m}^3$  to ppm:

$$\frac{X \text{ mg/m}^3}{\text{molecular weight}} \times 24.45 = Y \text{ ppm}$$

Example: 1  $\text{mg/m}^3$  of Ammonia, which has a molecular weight of 17, is equal to 1.44 ppm.

This equation is derived from the gas law,  $PV = nRT$ , and uses the fact that 1 mole of a gas occupies 24.45  $\text{dm}^3$  at 1 atm (760 mm Hg) and 25° C (24.04  $\text{dm}^3$  at 20° C ).









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