In Photoacoustic Spectroscopy (PAS) the gas to be measured is irradiated by intermittent infrared light of a specific wavelength. The gas molecules absorb some of the light energy and convert it into an acoustic signal, which is detected by microphones. PAS is an inherently very stable method for detection of gases due to the use of high quality microphones and offers outstanding sensitivity, linearity, repeatability and low drift.

Low drift is an important consideration for long term measurements. The high linearity offers the possibility of accurately measuring gases over a wide range of concentrations. These features makes the PAS method very suitable for the measurement of green house gases such as R134a, R152a and R744 as they are strong absorbents of infrared light and thus can be detected at very low levels.
Various gas detection techniques have been available for many years based on different detection principles with various levels of accuracy. However, common for most of them are that they require frequent calibration. One technique, Infrared Photoacoustic Spectroscopy, offers the advantage of infrequent calibration (few times a year) and a short analysis time.

The photoacoustic effect is based upon the conversion of light energy into sound energy by a gas, liquid or soil. It was discovered and investigated by Alexander Graham Bell in the late 1800’s, but was little more than a curiosity until 1970’s when there was a renewed interest due to the development of lasers and very sensitive condenser microphones. Since that time, photoacoustic based instruments have been used to monitor for a wide variety of chemicals used i.e. in the automotive industry.
The photoacoustic effect

Sequence of events

• gas sample is sealed in measurement chamber
• chamber is irradiated with pulsed, narrow-band light
• gas absorbs light proportional to its concentration and converts it to heat
• gas heats and cools as the light is chopped
• temperature fluctuations generate pressure waves
• pressure waves are detected by microphones

The photoacoustic effect is the emission of sound from an enclosed gas sample absorbing chopped infrared light. The type of light source most suited to gas detection and analysis is one, which emits radiation in the infrared region between 650 and 4000 cm\(^{-1}\). An excellent and more dependable alternative to sunlight is an incandescent source, a wire filament heated to a high temperature. The spectral output is continuous, with 70-80% of it in the infrared region. Narrow bandwidth radiation is required for spectroscopy and optical filters with a fixed bandwidth are used in conjunction with the infrared light source.

When a gas is irradiated with light, it absorbs some of the incident light energy. The amount of energy it absorbs is proportional to the concentration and the absorbed light energy is immediately released as heat and this causes the pressure to rise. When the light is modulated at a given frequency, the pressure increase is periodic at the modulation frequency and the sound waves are picked up by microphones.
This schematic drawing shows the measurement system in the gas monitor.

1. An air sample is drawn into the measurement chamber and the chamber is sealed by the valves.

2. Radiation from the IR-source passes through a chopper and optical filter into the chamber. The IR radiation is absorbed and generates heat and pressure variations.

3. The pressure variations correspond to the chopper frequency, creating a pressure wave which can be detected by the microphones.

4. The microphone signal, proportional to the gas concentration, is post processed and the measurement result is calculated.
A range of filters covers the mid IR range cover specific gases as well as a number more generic filters in the so called finger print region where specific gases have strong absorption.
Since water absorbs infrared light in the region covered by the optical filters, the photoacoustic monitor always compensates for water. The water content of the sample is measured by a special water filter which has a centre wave length at 1985 cm$^{-1}$ in a region where only very few gases absorb infrared light and interfere with the measurement.

The filters optimal for measurement of R134a, R152a and R744 are indicated on the figure. The are all placed in the range where the water absorption is relatively low causing a lower but not negligible interference.
Improved Accuracy with Water Compensation

Vapour Phase

No Water Compensation
The influence of 10,000 ppm water ~ Tdew of 7.4 °C (STP) in the sample:
UA0971: 0.4 ppm ~ 40 Detection Limits
UA0972: 0.5 ppm ~ 20 Detection Limits
UA0973: 0.5 ppm ~ 10 Detection Limits
UA0982: 7.5 ppm ~ 20 Detection Limits

With Water Compensation
Water Compensation removes >98% of residual error.
UA0971: 0.08 ppm ~ 0.8 Detection Limits
UA0972: 0.01 ppm ~ 0.4 Detection Limits
UA0973: 0.01 ppm ~ 0.2 Detection Limits
UA0982: 0.15 ppm ~ 0.4 Detection Limits

The four filters water sensitivity to 10,000 ppm of water is shown in the table and together with the corresponding number of detection limits. Since the contribution of water is independent of the actual gas concentration, the impact is highest at low gas concentrations. Water compensation can remove more than 98% of the error assuring a very accurate measure of the concentration. One other method to minimise the effect of water interference is to calibrate the gas with a known content of water, however any deviations from this content in real life will affect the accuracy.
Microphones are extremely sensitive. At the detection limit, typical values are:

- Temperature change: $10^{-8}$ K
- Pressure change: $10^{-5}$ Pa
- Membrane deflection: $10^{-14}$ m

If an absorbing gas is present in the measurement chamber at a concentration close to its detection limit (ppb range), the temperature increase in the chamber is typical $10^{-8}$ K. The corresponding pressure increase is approximately $10^{-5}$ Pa and this deflects the membrane of a $\frac{1}{2}''$ microphone by only $10^{-14}$ m; a distance slightly greater than the diameter of an electron.

The advantage of using a microphone is its high stability which at room temperature has a theoretical change of less than 1% in 250 years.
In conventional transmission spectroscopy, light passes through the measurement chamber and a light detector measures the amount of light transmitted through the cell. At very low concentrations, the difference between two almost equal signals is being measured and the signal to noise ratio is poorer with transmission spectroscopy than with PAS, and therefore is a less sensitive technique.

PAS is a more accurate technique than transmission spectroscopy as it measures the absorption directly.
Advantages of PAS

The PAS technique is built into the stationary Photoacoustic Multi-gas Monitor 1314 and the portable Photoacoustic Field Gas-Monitor 1412. Some of the advantages and characteristics of infrared photoacoustic spectroscopy as it pertains to trace gas monitoring are as follows.

- High sensitivities can be obtained. Instruments using conventional infrared light sources such as heated Ni-Chrome wires have demonstrated detection limits in the low ppb to ppm range for single gases.
- Photoacoustic based instruments are very stable, primarily due to the stability of the microphones. This means a very stable base line and virtual no zero drift.
- A dynamic range of up to 5 orders of magnitude relative to the detection limit for a particular gas can be achieved. Thus, very high concentrations can be measured with a single instrument i.e. from 1ppm to 100,000 ppm.
- Simpler instrumental and optical set-ups can be used. In particular, multipass gas cells are not needed, thus eliminating the problems of maintaining optical alignment through this type of cell.
- The low range-drift enables measurements to be performed of long periods of time with a reproducibility of 1% of the measured value and with a range-drift ±2.5% of the measured value in three months.
Numerous Applications

- Animal Husbandry
- Atmospheric Research
- Automotive
- Contaminated Soil
- Ethylene Oxide Sterilisation
- Fermentation
- Food
- Formaldehyde
- Fuel Cells
- Gas Manufacturing
- Green House Gases
- Headspace
- Hospitals
- Indoor Air Quality
- Industrial Hygiene
- Photocatalysis
- Photographic Industry
- Power Industry
- Semiconductor
- SF₆ in Transformers
- Solvent Recovery
- Thermal Comfort
- Vent Emission
- Ventilation
- Warfare Agents
- R134a in MAC systems

The use of the PAS technique is widely accepted within numerous applications covering various types of industries. A number of these applications are related to the testing of vehicles and its components.
Also outside the automotive industry leakage testing is done using the PAS technique. In the power industry PAS is used for SF₆ leakage testing of high voltage switch gears based on a similar method used for MAC leakage testing.
Automotive Applications

• Test chamber calibration with leak standard
• Characteristics of hose permeation
• Relative contribution of hose permeation
• Transient emission rates
• Leaks from couplings, joints and service ports
• Leaks from compressors and heat exchange
• Ethanol exhaust and evaporative emissions in vehicle
• Evaporative measurements of R134a
• Ventilation measurements
• Thermal comfort in vehicles

PAS has proven its strength within several MAC and other automotive test applications.
Based on a request from a vehicle manufacture, EPA and CARB have approved the use of Photocoustic Spectroscopy for measurements of Ethanol exhaust and evaporative emissions instead of using impingers samples and gas chromatograph.
Detection Limits for Relevant Gases

- 0.01 ppm for R134a using UA0971
- 0.002 ppm for R152 using UA0972
- 1.5 ppm for R744 using UA0982*

*) other filters are available for different ranges.

The PAS technique assures low detection limits for the gases of interest in MAC testing. For R744 (CO₂), other filters are available for higher and lower ranges.
Delphi Thermal & Interior Technical Center, Lockport, NY is using the Photoacoustic Multi-gas Monitor 1314 in their laboratory for measurements of R134a, R152a and R744. This new test procedure using photoacoustic has proven to be accurate and time saving compared to alternative methods. The Photoacoustic Gas-Monitor 1314 is well suited for these types of laboratory measurements. The monitor is easily operated and can measure up to 5 different gases within 70 seconds including compensation for water vapour. If only one gas is measured the sample interval is 40 seconds allowing detailed analysis.
Example of a hose permeation test performed by a customer.
Detail from the previous slide showing 100 individual measurement points.
To prove the linearity of the Photoacoustic Gas Monitor, General Motors has tested it using a NIST calibrated Gas Divider at different concentrations of R134a in the range from zero to ten ppm and found it to be 100% linear.
When performing long term measurements the stability is also of great importance. This figure shows the zero drift in an experiment performed by GM on R134a.
Another application of PAS is ventilation measurements in vehicle cabins. By use of the tracer-gas technique it is possible to evaluate the performance of the ventilation system in the vehicle. This is normally a very time consuming task, however, when using the tracer-gas technique these measurements can be performed both quickly and precise. It is possible to measure the overall performance of the ventilation system at different settings on the control panel and measurements can be conducted both in the laboratory or on the road while driving simulating actual conditions at various driving velocities.
Above measurements were performed in a vehicle while driving on the road at different velocities. The total volume flow of the ventilation system is shown as a function of driving velocity at different fan speeds.
A more detailed analysis of the individual performance of each vent can also be performed. A task which is very time consuming if at all possible using other techniques.
Another very important application within the automotive industry, but not related to the use of the PAS technology, is the evaluation of thermal comfort in vehicles and other means of transportation. A new standard ISO 14505 deals with the assessment of thermal comfort in vehicles using the equivalent temperature. One of the tested and approved methods in this standard is the use of a Dry Heat Loss Transducer measuring the equivalent temperature. With a number of transducers mounted on a man shaped manikin the weighted equivalent temperature can be calculated and used for evaluation of the level of thermal comfort inside the vehicle cabin.
In this experiment the equivalent temperature is measured in six different positions. The light blue colored line indicates the weighted mean equivalent temperature based on the area each transducer represent of the total body area.