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PROGRESS IN FIBRE-REMOTED GAS CORRELATION SPECTROMETRY

J.P. DAKIN* **and H.O. EDWARDS**

Optoelectronics Research Centre
University of Southampton
SO9 5NH, U.K.

Abstract

The paper reports on progress on gas sensing using real-time correlation spectroscopy, where a gas is used to "recognise" its own spectral absorption lines. Our recent results on methane detection using pressure modulation spectrometry are shown, and a new method of modulating the absorption of the gas in the reference cell section of an ammonia detection system is reported for the first time. The basic concept of correlation spectrometry involves the passage of light sequentially through two gas cells, a reference cell containing a known quantity of the gas to be detected, and a sampling cell where the presence of the gas is to be determined.

An optical signal passing sequentially through the cells will suffer absorption in each of the cells. If the absorption in the reference cell is periodically modulated, then the total absorption depends on whether the gas absorption lines in the sampling cell correlate with those in the reference cell gas. If the absorption lines of the gases do not correlate strongly, then the modulation index of the optical signal is essentially unaffected by the presence of the different gas in the sampling cell. Therefore, the concentration of a specific gas in the sampling cell can be quantified by this means.

Pressure modulation of the gas within the reference cell is achieved by the use of a novel acoustic resonator. This device provides a reasonable pressure ratio whilst being compact and easily driven. Unlike previous piston-compressors, the high modulation frequency of the resonator improves the tolerance to transients in the optical signal produced by the passage of dust through the optical beam. The system can be tailored to detect a desired gas by changing the reference gas and a broadband section filter. Results for methane are presented in this paper. A novel method for detection of ammonia gas is reported for the first time. This involves Stark modulation of the gas in the reference cell, by the application of an electric field. This method is applicable to gases with strong electric dipole moments, such as NH_3, CO, NO_x and HCl.

* Certain of the ideas in this paper were generated whilst J.P. Dakin was at YORK Biodynamics Ltd, Itchen Abbas, Hants. U.K.

Introduction

Gas detection is an essential requirement for environmental monitoring, industrial control and for assessment of gas-explosion hazards. Many common gases exhibit fundamental optical absorption spectra in the infra-red region, with weaker overtone bands extending into the near infra-red and visible. These absorptions arise from vibration-rotation interactions within the molecule, so the characteristic spectral lines provide a means of 'fingerprinting' a gas. For example, analysis of the optical absorption through a gas mixture permits identification of both the composition and concentration.

The use of an optical fibre link to the optical absorption cell was first proposed by Inaba[1]. Low-loss fibres allow the sensor head to be sited remotely from the monitoring station, and offer the possibility of multiplexing a number of sensors. However, conventional silica fibres have the disadvantage that transmission is restricted to the near infra-red region, so only the weaker overtone bands can be monitored. In the future, fluoride fibres may extend operation further into the infra-red.

Conventional gas sensing techniques using fibres involve probing the gas at one wavelength within the absorption spectrum, with a second source, at a wavelength removed from the absorption band, as a reference. However, the drawback with this scheme is that any contaminant gases showing absorption at *either* probe *or* reference wavelengths will disturb the measurement. Also, the signal change due to absorption by the weak overtone bands is usually small, and this limits sensitivity.

An interesting technique aimed at the remote monitoring of planetary and terrestrial atmospheric gases was demonstrated by Goody[2], and further developed by Taylor[3]. In this scheme a periodic pressure modulation is applied to the gas contained in a reference cell. The absorption lines in the reference cell correlate with the absorption lines of the same gas (if any present), in a sampling cell at the sensor head. The principle of pressure modulation spectrometry is described in more detail below. Both authors referenced above proposed a bulk optical system to analyse sunlight transmitted through the atmosphere. A low frequency (15Hz) piston compressor was used to provide the pressure modulation.

In this paper, we report, for the first time, the use of the pressure modulation technique, in conjunction with an optical fibre network, for the remote monitoring of a passive gas sensing cell. The pressure-modulated reference cell used a novel acoustic resonator to enable a high modulation frequency to be employed. Compared with the piston-compressor, our approach eliminates mechanical vibration, and because of its higher frequency of modulation, provides greater tolerance to transients due to the passage of dust particles through the optical path. The acoustic cell is inherently less complex, is more easily driven by electronic circuitry and requires no sliding gas seals.

The remote fibre gas sensor has been tested with a number of gases; here results on methane detection will be presented in view of the importance of environmental methane sensing. The prototype demonstrated is capable of detecting gas concentrations well below the lower explosive limit for methane. A noise-limited sensitivity of 50ppm makes the device suitable for a wide range of applications where gas-explosion risk must be monitored.

Principle of Pressure Modulation Spectrometry

Methane has a vibration-rotation absorption overtone ($2\nu_3$ band) conveniently centred at 1.66μm in the low-loss region for silica fibre. The methane absorption spectrum is shown in Figure 1, together with the transmission curve for the interference filter used to select this operational band. The system (Figure 2) consists of two gas cells, a sampling cell (measurement cell) and a reference cell linked via optical cables. The sampling cell is located at the remote measurement site, and comprises a multiple-pass White[4] cell, to achieve a large interaction length with the gas. The second cell (the pressure modulated reference cell) is filled with pure methane,the reference gas. Within this cell, the gas is subjected to a sinusoidal pressure modulation in order to modify its absorption.

The detected signal D(C,t) is given by Equation 1, integrated over the bandwidth of the optical selection filter. The amplitude of the signal varies with the gas concentration C in the sampling cell, whose transmission is given by $T_1(\lambda,C)$. The optical transmission $T_2(\lambda,t)$ of the second cell is time-varying due to the applied pressure modulation of the reference gas contained in this cell. The launched power spectrum is given by $S(\lambda)$, the detector spectral response by $R(\lambda)$, and $T_s(\lambda)$ is the overall transmission of the system.

$$D(C,t) = \int_{filter} S(\lambda) \cdot T_1(\lambda,C) \cdot T_2(\lambda,t) \cdot T_s(\lambda) \cdot R(\lambda) \cdot d\lambda \qquad (1)$$

The absorption lines in methane are strong and distinct at normal temperature and atmospheric pressure. Under these conditions, the linewidth is related to the pressure, and is primarily determined by molecular collision rather than Doppler broadening (i.e. pressure broadening).

A periodic pressure modulation imposed on the gas affects the overall absorption of the gas in the modulation cell by changing both the line strengths and widths across the band. The pressure change causes a localised change in the gas concentration, and hence modulates the peak absorption of the gas lines. In addition, the linewidth of the absorption lines is modified due to increased collision broadening as the pressure is modulated. The combination of the two effects results in periodic modulation of the integrated absorption across the band, which is in phase with the applied pressure variations. Consequently, an alternating signal is superimposed on the transmitted optical level.

If the gas sample introduced into the White cell correlates with the absorption lines of the gas contained in the modulation cell, then light is selectively removed from the spectrum before passing through the modulation cell. The result is to *reduce* the amplitude of the alternating signal occurring in response to the applied pressure modulation. Therefore, the signal level *falls* in relation to the gas concentration in the White cell. Any contaminant gas which does not have a substantial correlation with the gas lines in the modulation cell will affect the signal to only a small extent. This fact accounts for the good selectivity of the pressure-modulation technique, since each gas has a unique spectrum.

Novel Pressure Modulation Cell (Acoustic Resonator)

Our pressure-modulation cell consists of a cylindrical-cavity resonator with an optical window close to one end to allow the optical beam to pass through the gas. Situated at the opposite end is a flexural piezoelectric diaphragm (Unimorph[5]) which excites standing acoustic waves in the cavity. The cell is dimensioned such that the cavity length corresponds to one half of the acoustic wavelength in the gas. This creates a resonant cavity which supports a standing acoustic wave with pressure maxima at each end. The lateral dimension of the cell is sufficiently small to avoid standing transverse waves, so the gas region traversed by the light beam has an essentially constant pressure ratio. The cavity resonator had a quality factor of 90, and was designed to operate at the resonant frequency of the Unimorph (2.5kHz). Despite the lower pressure ratio, defined as the ratio of RMS deviation to mean pressures, achieved with the acoustic resonator (0.088 as opposed to 0.23 for the piston compressor), it is adequate to demonstrate a methane sensor with good sensitivity.

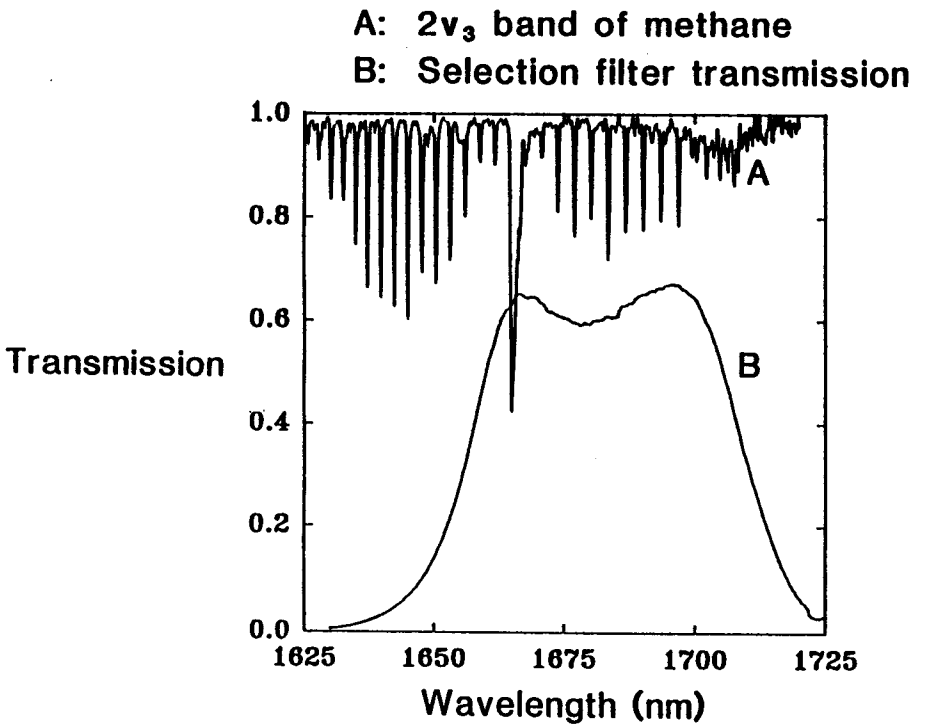

Fig 1 Transmission spectra
(A) methane (100%, 10cm path)
(B) optical selection filter

Experimental Results

The experimental configuration employed for the methane detector is shown in Figure 2. The multi-pass White cell arrangement used in the sensor head directed a beam twelve times through the gas to be analysed, resulting in a total optical path length of 4.8m. Multimode (100/140μm) fibre, compatible with industry standard, was used throughout the system to maximise the optical power level. The fibre-guided output from the sampling cell was passed through the modulation cell on its path to the detector. A total fibre length of approximately 20m was used to demonstrate the system, although kilometre lengths would only degrade the signal by a few dB. The optical power received at the quantum-noise-limited detector was 0.25μW. The pressure modulation cell was filled with pure methane, and had an internal optical path length of 36mm.

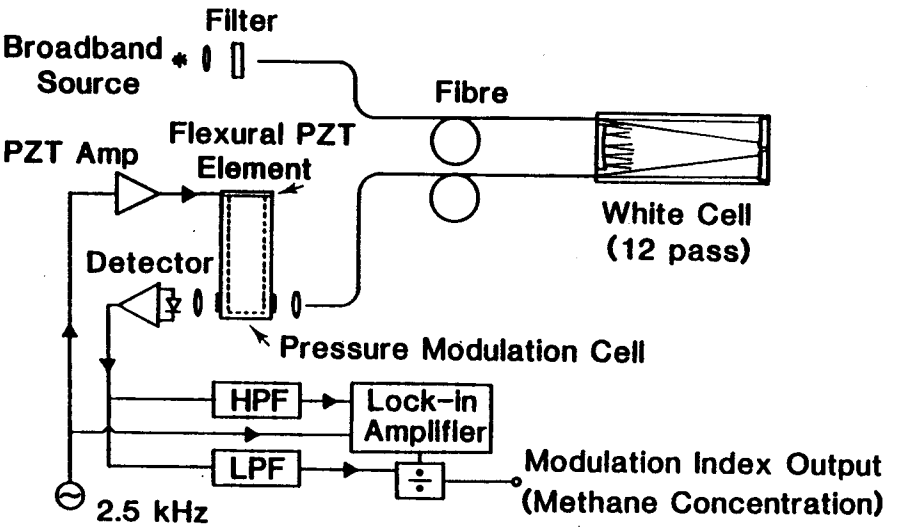

Fig 2 Experimental configuration

The signal from the optical receiver consists of a small, approximately sinusoidal modulation superimposed on a continuous voltage level. It is convenient to define the performance of the system in terms of a modulation index, given by the ratio of the alternating peak-to-peak signal to the D.C. voltage. The post-detection signal processing involves synchronous detection of the alternating signal and subsequent normalisation with respect to the D.C. level to provide referencing for any fluctuation in optical source power or system attenuation.

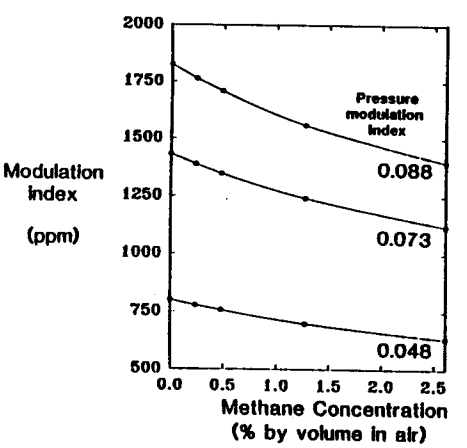

Fig 3 Calibration curves for methane

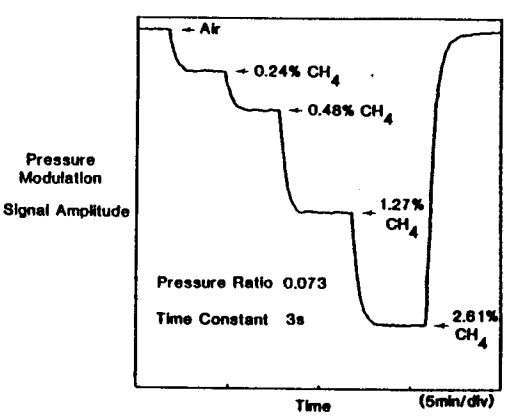

Fig 4 Response to methane/air mixtures

Calibration of the sensor was performed by sequentially filling the White cell with a range of standard methane/air mixtures. The resulting modulation index was recorded for a range of pressure ratios in the modulation cell, and is given in Figure 3. The systematic measurement error in the modulation index figure is currently 2%. Illustrated in Figure 4 is the variation in signal as a range of methane dilutions were introduced into the sampling cell. As can be seen from the trace, the stability of the system is excellent, even for this early result. Any systematic variations in signal level appear to be primarily due to a change in the pressure ratio resulting from drift in the tuning of the modulation cell with temperature.

The lower explosive limit (LEL) for methane in air occurs for a concentration of 5% methane by volume. Clearly, the detector has no difficulty in discerning methane levels well below this value. The detection limit is ultimately determined by the point where the signal becomes equal to the detector noise plus any systematic drift. The measurement bandwidth, and hence the random noise level, is governed by the time constant of the lock-in amplifier. Taking a time constant of one second yields a noise-limited sensitivity of better than 50ppm methane by volume, or 0.1% of LEL.

Cross-sensitivity to contaminant gases which have absorption bands in the same spectral region as methane should be small with the pressure modulation scheme. This was assessed for the system by introducing ethane into the sampling cell, whilst retaining methane in the reference cell. Of the likely contaminant gases, ethane has the most similar absorption spectrum to methane, and most other gases are expected to show less correlation with methane. As calibrated dilutions of ethane were not available, a new set of results was taken firstly with pure (100%) ethane and then with pure methane, using a shorter sampling cell length of 0.105m for these more concentrated samples. The response to ethane was found to be 8% of that of methane, with ethane having an integrated absorption which was twice that of methane in this system. In contrast, for a conventional broadband system, the unwanted gas, ethane, would thus give twice the signal of the desired gas, methane. Our system therefore provides approximately 25 times better selectivity than a conventional broadband scheme.

Stark Modulation Spectroscopy (SMS)

It would be convenient to have a non-mechanical means of changing the absorption of a gas. In view of this, the concept of Stark modulation spectroscopy was devised. For certain specific gas types, this represents an easier way of modulating the spectra without need for mechanical influences.

If the gases to be detected have molecules with an assymmetric electrical distribution (i.e. they have an "electrical diple moment"), then their absorption lines can be modulated merely by applying a strong electrical field (See Fig 5). Rather than a change in the depth of the absorption lines, as occurred with pressure modulation, the application of electric field causes a broadening or splitting of the fine spectral lines as a result of the well-known Stark effect (See Fig 6).

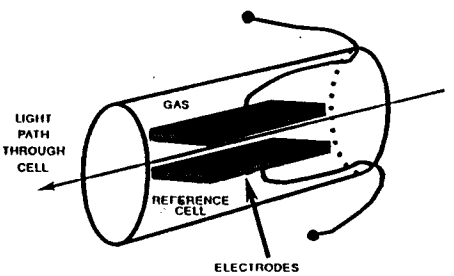

Fig 5 Schematic of Stark modulation cell

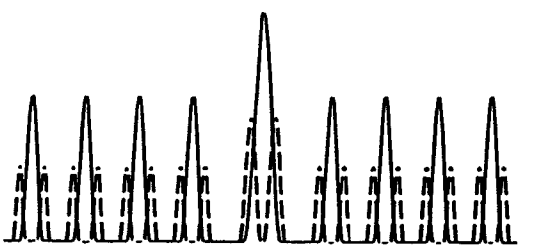

Fig 6 Schematic illustration of the spectral line splitting due to the Stark effect (solid lines show gas spectrum before field is applied, dotted lines with electric field)

This splitting affects the degree of overlap between the absorption spectra of the gas reference sample (to which the electric field is applied) and the absorption spectrum of any gas in the measurement region.

The advantages of the SMS method are its exteme simplicity and the fact that, in the absence of any gas in the detection or measurement region, there is little change in detected signal as the applied electric field is changed. The disadvantages of the method are that a high voltage must be applied to the electrodes in the gas cell and the method is only applicable to gases with polar molecules (e.g. NH_3, CO , NO_x, HCl). Nonetheless, it is believed this may be a very cost effective way of sensing relatively high concentrations of the above gases.

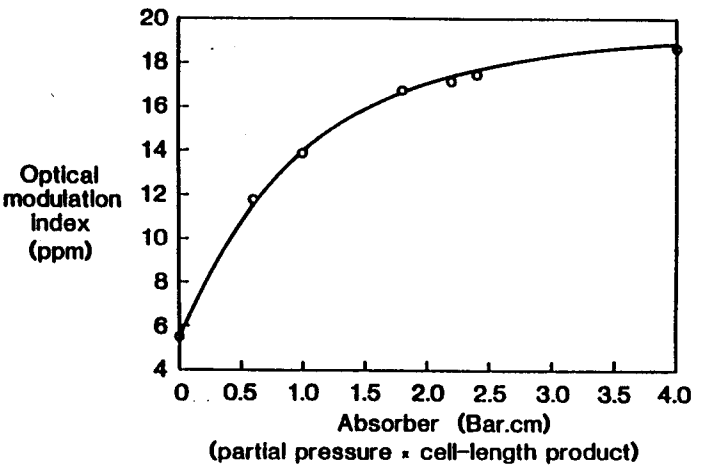

Fig 7 Response of Ammonia Sensor using Stark Modulation Spectroscopy

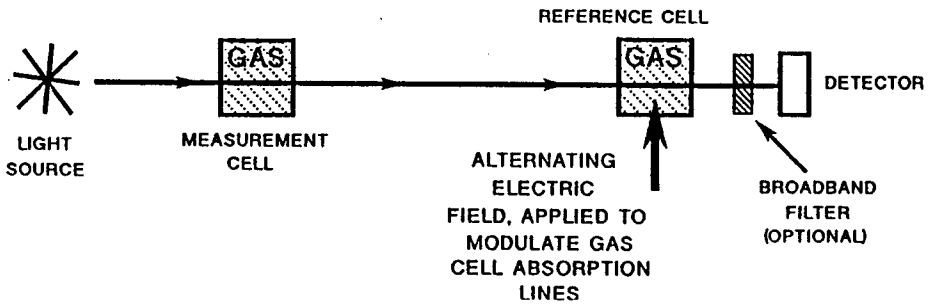

Fig 8 Gas sensing system, using real-time correlation spectroscopy, with reference cell modulated by application of electric field. (Cell is stark cell, as shown in Fig 5)

The method has recently been successfully tried with ammonia gas, where concentrations in the range 1% to 10% have been measured in a cell of 40 cm path length (See Fig 7). This measurement was performed with a system of the type shown schematically in Fig 8. These are only preliminary results, and it is expected to be possible to measure to 0.1% or less in future.

Conclusions

We have demonstrated, for the first time, a novel fibre-optic-remoted gas measurement system based on pressure modulation spectroscopy which uses a new design of pressure-modulation cell based on an acoustic resonator. This methane sensor was capable of a noise-limited sensitivity of 50 ppm, using an optical path of 4.8 metres. In addition, a novel Stark-modulation system for the detection of gases with high electrical dipole moments has been reported for the first time. Although this system is much newer, it has been successfully demonstrated using ammonia gas in the range of 0 to 10%. Both systems are inherently simple, highly selective and can be reconfigured to measure other gases merely by changing the gas in the reference cell and by changing the bandpass filter to correspond with the appropriate absorption band. They are compatible with broadband LED or white-light sources and multimode fibre. Moreover, it is possible to pick out individual components of a gas mixture using separate detection systems with appropriate reference-gas cells.

References

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