

## Detection of Gases and Gas Mixtures by Correlation Spectroscopy

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### Abstract

This paper describes the detection of various common gases by means of Correlation Spectroscopy, employing a Complementary-Source-Modulation (CoSM) approach based on compact light-emitting diode (LED) sources. Theoretical results for the quantitative detection of O<sub>2</sub>, CO, and CO<sub>2</sub> by this CoSM method are presented, using, as their basis, spectral absorption data from the Hitran database. In demonstrating the proposed detection principle, new experimental results for the detection of O<sub>2</sub> in air are presented, with the use of practical low-cost LED sources.

**Keywords:** Correlation spectroscopy; optical absorption; gas detection; oxygen; carbon monoxide; carbon dioxide.

### 1. Introduction

The reliable detection and monitoring of gases and gas mixtures plays a crucial role in many real-world environmental and industrial applications. This may involve, for example, the monitoring of gas species of relevance for health and safety issues, or the real-time monitoring of gaseous products and by-products in an industrial process. When considering such applications, it is of great importance to develop sensing techniques which are quantitative, are not susceptible to poisoning, are unaffected by contaminants, and are specific to a target gas in a mixture. It is particularly advantageous if the methods employed are not

only reliable, but can also be configured in a self-checking arrangement. Ever-more stringent monitoring requirements, in a variety of application areas, fuel the strong need for ongoing research on this topic.

Many common gases exhibit their fundamental optical absorption in the infra-red region, but some (eg. oxygen and chlorine) have electronic bands in the visible region. A number of systems for the detection of gases and gas mixtures have been devised, based on optical absorption methods [1, 2, 3, 4]. However, in many instances, these techniques of broadband optical absorption are not entirely suitable for real-world applications, primarily because of fundamental issues relating to poor selectivity (possible overlap of absorption bands). Even using narrowband laser sources, there can be other problems due to coherence effects. On the other hand, methods such as correlation spectroscopy [5, 6, 7, 8, 9], which take advantage of the full multi-line structure of the target gas are attractive. They offer the desired selectivity yet still retain appreciable sensitivity. Such an approach is particularly useful for monitoring the presence of a gas, or even a number of individual gases within a mixture, using a common sensing instrument. In addition, the potential of this technique for real-time monitoring applications is implicit.

In this paper, we present new theoretical simulations for the detection of O<sub>2</sub>, CO, and CO<sub>2</sub> gases using our proposed Complementary-Source-Modulation (CoSM) method of real-time correlation spectroscopy, first reported earlier [10]. These new calculations are based on freely-available spectral data from the Hitran database ([www.hitran.com](http://www.hitran.com)). The CoSM approach, shown in Fig. 1, involves the modulation of two light sources in anti-phase, passing light from one of these sources through a reference cell containing the target gas (or gases) of interest for detection, and then combining this now-partially-absorbed light beam with a proportion of unaffected light from the other source, such that there is now no net intensity modulation. This combined beam is then used to probe for the target gas. As the beam component which has passed through the reference gas sample now has less available optical

energy within the narrow spectral region of the target gas spectral absorption lines, a net intensity modulation of the combined beam will now be restored as it passes through a measurement cell containing the specific target gas. In our arrangement, it is the intensity modulation index (ratio of AC component to mean DC component) of this final detected signal, after passing through the measurement cell, which is a measure of the gas concentration. A key feature of this approach is that it is only differential absorption between the two beam components that leads to a modulation of the measurement signal. Thus, the presence of a contaminant with non-matching spectral lines will not affect the measurement in the real-world environment.

## FIGURE 1

Apart from the theoretical calculations, a bench-top, fibre-coupled, CoSM system has been constructed, which has the potential to detect a variety of gases using simple low-cost light emitting diode (LED) sources. The sources in this arrangement are driven via an input/output (I/O) card and PC controller, and the measurement signal intensity modulation is also recovered via analogue inputs on the I/O card, and then processed by the same PC. We believe it is the first time oxygen has been sensed in this manner, combining the selectivity of correlation spectroscopy with the use of compact low-cost semiconductor sources and detectors. This cost-effective yet efficient approach, combined with the potential for remote measurement cell location interrogated via a single optical cable, suggests attractive commercial potential for the device.

## **2. The Complementary-Source-Modulation Approach**

### **2.1 Basic Method**

A manifold of narrow spectral absorption lines is often unique to a simple gas molecule and, as such, present an identifiable 'finger print' of the gas species. The underlying principle of our correlation spectroscopy approach involves a comparison of the absorption spectrum of a

particular reference gas of interest relative, to that of a gas to be measured, and using this to identify the presence and concentration of the gas in the unknown mixture. An arrangement illustrating this approach for a bulk-optic system is that given in Fig. 1. In practice, an initial differential spectral-absorption modulation is achieved by an arrangement whereby the beam before the measurement cell is periodically switched between two different light paths: light from two spectrally-similar light sources is combined after passing one beam through a reference gas and the other not. The switching is facilitated by driving the two sources in anti-phase, and a balance of the relative intensities is achieved by adjusting the level of the respective drive current amplitudes (for the case of LED sources). In this way, the net intensity modulation of the combined beams is set to zero before it is passed through the measurement cell.

A consequence of this arrangement is a beam of two temporally-diplexed components of similar net intensities. Most importantly, the light component which passed through the sample of gas in the reference cell will contain less light on the spectral absorption lines specific to the gas, having, at each specific wavelength, lost energy in accordance with Lambert's law. Thus, if the combined beam experiences a wavelength-independent optical absorption in the subsequent measurement cell, the two beam components are similarly absorbed and there is therefore no change in their relative intensities. On the other hand, should this beam pass through a gas having absorption lines which match that in the reference cell (i.e. the target gas) the component which has not originally passed through the reference cell experiences greater attenuation. Thus, there is now an intensity modulation of the final output beam. After passing through the measurement cell, the beam in our arrangement is finally directed onto an optical detector by means of which the intensity modulation is ascertained. When this modulation component is divided by the mean DC optical intensity, an intensity modulation index is found and a useful quantitative measure of the gas concentration is achieved.

The arrangement given above forms the basis of the model used for our theoretical analysis for a few select gases. In an extension of this arrangement, an experimental fibre optic version, suitable for remote measuring via fibre cable, is described in Sect. 4 and results of O<sub>2</sub> detection are presented.

## 2.2 Theory

The following discussion illustrates the manner in which the change in detected intensity modulation index of the complementary-modulated sources may be related to a quantifiable concentration of the desired gas species in the measurement cell. In its simplest sense, the method involves passing of light from a source, with spectral intensity  $P(\lambda)$ , firstly through a reference cell of transmission  $T_1(\lambda)$ , and secondly through a measurement cell of transmission  $T_2(\lambda)$ , before impinging on a detector of spectral responsivity  $R(\lambda)$ . In addition, there may also be a filter, with transmission  $F(\lambda)$ , inserted in the system in order to narrow the effective spectral band to one appropriate to cover the gas absorption band (or manifold of lines) to be monitored. The detected signal  $I_{\text{det}}$ , after passage through these optical elements or cells, is given by<sup>1</sup>:

$$I_{\text{det}} = \int P(\lambda)T_1(\lambda)T_2(\lambda)F(\lambda)R(\lambda)d\lambda \quad (1)$$

Of the functions contained in this expression, well-tabulated values for  $T_1(\lambda)$  and  $T_2(\lambda)$  are available for many common gases from the Hitran database, and the source, detector, and filter spectra may be readily obtained, either from the respective manufacturer's specification data sheets or from our own on-site measurement.

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<sup>1</sup> It is the nature of the integrals of  $T_1(\lambda)T_2(\lambda)d\lambda$  over a wavelength range that gives rise to the 'correlation spectroscopy' description of the method, as this type of integral is the numerator in the standard definition of the mathematical correlation function.

In our CoSM scheme, it is the intensity modulation index of the final signal that is of interest for the gas detection and hence for calculation of the expected system response. If one assumes that the combined beam components enter the measurement cell in such proportion that there is no net modulation, then the two beam components after this measurement cell give rise to signals of:

$$A \int P(\lambda) T_2(\lambda) F(\lambda) R(\lambda) d\lambda \quad (\text{Signal component not passed through the reference cell}) \quad (2)$$

and

$$\int P(\lambda) T_1(\lambda) T_2(\lambda) F(\lambda) R(\lambda) d\lambda \quad (\text{Signal component passed through the reference cell}) \quad (3)$$

where  $A$  is a scalar accounting for beam attenuation in the reference cell. From these, the difference between these beams may be expressed as:-

$$\int P(\lambda) T_1(\lambda) T_2(\lambda) F(\lambda) R(\lambda) d\lambda - A \int P(\lambda) T_2(\lambda) F(\lambda) R(\lambda) d\lambda \quad , \quad (4)$$

and the modulation index, a normalised, unitless, fraction, simply derived by dividing the AC component of the detected signal by the mean DC signal, is given by:-

$$\frac{2 \left( \int P(\lambda) T_1(\lambda) T_2(\lambda) F(\lambda) R(\lambda) d\lambda - A \int P(\lambda) T_2(\lambda) F(\lambda) R(\lambda) d\lambda \right)}{\int P(\lambda) T_1(\lambda) T_2(\lambda) F(\lambda) R(\lambda) d\lambda + A \int P(\lambda) T_2(\lambda) F(\lambda) R(\lambda) d\lambda} \quad (5)$$

This analysis forms the basis of the theoretical approach we have applied when considering the gases selected in Sect. 3. Because the light sources used are generally broader than the spectral region covering the manifold of strong gas absorption lines, and because the detector response is also relatively flat over this region, we have, in most cases, assumed the functions  $P(\lambda)$  and  $R(\lambda)$  are constants of value  $P$  and  $R$ . The main remaining spectral variation in the above equations is therefore that of the filter  $F(\lambda)$  and that of the gas cells  $T_1(\lambda)$  and  $T_2(\lambda)$ , greatly simplifying the calculations.

### **3 Theoretical Prediction of the Correlation Intensity Modulation Index for Various Common Gases**

In Figs. 2 to 10 we present data and results relating to the application of the CoSM detection approach to the gases O<sub>2</sub>, CO, and CO<sub>2</sub>. In the first three of these, we show the spectra for the respective gas species, as derived from the Hitran spectral-absorption database and analysed using commercially-available HitranPC software<sup>2</sup>. The absorption bands analysed in this paper, centred at 0.761 μm, 1.568 μm, and 2.01 μm, for O<sub>2</sub>, CO, and CO<sub>2</sub> respectively, were chosen, not because they necessarily represent the strongest absorption lines for the respective gases, but on account of their optimum suitability for a detection system employing conventional optical fibre components.

**FIGURE 2**

**FIGURE 3**

**FIGURE 4**

Shown in Figs. 5 to 7 are intensity modulation index results for O<sub>2</sub>, CO, and CO<sub>2</sub>, derived by means of numerical integration of the spectral data over the wavelength range, in conjunction with eqn. (5).

**FIGURE 5**

**FIGURE 6**

**FIGURE 7**

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<sup>2</sup> Ontar Corporation, New Andover, USA

For the case of these gases, a rectangular (or so-called 'top-hat') transmission functions  $F(\lambda)$  has been assumed for the filter at  $0.7610 \pm 0.0015 \mu\text{m}$ ,  $1.5684 \pm 0.010 \mu\text{m}$ , and  $2.010 \pm 0.040 \mu\text{m}$  for  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$  respectively. The results are also presented on logarithmic scales in Figs. 8 to 10, so a wider dynamic range can be covered using the log scales. Clearly the extent of any non-linearity at high gas concentrations can be observed more readily on the linear scales.

**FIGURE 8**

**FIGURE 9**

**FIGURE 10**

It is clear, from these spectral plots and calculations, that, if the analysis is restricted to a narrow spectral range close to the peaks of the gas absorption curve, then the intensity modulation index is increased, and there is thus an effective improvement in the contrast of the measurement. At the same time, however, there is also a reduction of the overall light available for detection. Furthermore, if the filtering leads to a loss of useful absorption lines, then one of the major advantages of the correlation approach is lost; that of simultaneously measuring on many gas lines. Our compromise is to restrict the analysis to cover the major spectral bands, choosing the one for each gas that includes most of the stronger lines.

It can be seen, from the linear plots of modulation index versus gas concentration, that there is substantial non-linearity in the expected  $\text{CO}_2$  modulation index at high concentrations. This may be expected due to the reasonably high absorption of this gas in the  $2.01 \mu\text{m}$  band. By contrast, the non-linearity for  $\text{CO}$  and  $\text{O}_2$  is negligible, except for the region close to 100% concentration of  $\text{CO}$ . For most applications, it is highly unlikely that any of these non-linear regions would be of consequence for practical measurements, even for  $\text{CO}_2$  where the non-linearity commences at lower concentrations. It should be noted that all our simulations are



taken at a room temperature of 296 K and at a total pressure of 760 mmHg. We propose to study the smaller effects of likely changes in ambient temperature and barometric pressure at a later date.

#### 4. Experimental Measurement of Oxygen

The arrangement used for our experimental investigation of O<sub>2</sub> detection is shown schematically in Fig. 11. This makes use of low-cost LED light sources (Epitex L760-06AU) the outputs of which are coupled to 440  $\mu\text{m}$  large-core-diameter optical fibres – in the one case after being collimated and traversing a reference gas cell. An all-fibre 3 dB coupler (coupler 1) is used to combine these two beams, whilst a second such coupler (coupler 2) is used to direct a fraction of this combined beam to a reference detector in one arm, and another fraction to and from a collimated measurement gas cell in the other arm. The measurement detector can be placed at the end of the measurement cell, but it may also be placed at the return arm of coupler 2 if use is made of a retro-reflector at the end of the measurement cell [11]. Such an arrangement is shown in Fig. 12. Both optical detectors are inexpensive silicon-type photodiodes (Integrated Photomatrix Ltd. 10530DAL photodiode) integrated with in-package transimpedance amplifiers.

#### FIGURE 11

#### FIGURE 12

The addition of an interference filter, contained within the dual lens-collimator optics, positioned in the network between the two fibre couplers, is used to pre-select the required region of the LED spectra for O<sub>2</sub> sensing. In this instance, we have tuned a 765 nm filter of 3 nm FWHM bandwidth (CVI Laser Corporation F03-765.0-4-1.00 filter) by tilting it to bring it to a new central wavelength of 760.8 nm. Typically, the light intensity at the reference detector is of the order of 100  $\mu\text{W}$ , whilst that at the measurement detector is 70 $\mu\text{W}$ , when

placed at the end of the measurement cell or  $25 \mu\text{W}$  when placed on the return arm of the coupler 2 (i.e. the retro-reflected configuration). When implementing the arrangement, the modulation index of the combined signals monitored by the reference detector is set to zero by careful adjustment of the relative LED drive currents. Both this signal, and that of the measurement detector, is monitored by a PC-based lock-in amplifier, which triggers at the LED switching frequency of 1 kHz. Our chosen lengths of reference and measurement cells are 1000 mm and 800 mm, respectively, and the beam-waist diameter of the collimated light when passing through these cells is 25 mm.

The retro-reflective measurement cell arrangement is particularly attractive; firstly, because it facilitates the remote placement of the measurement cell, with interrogation via a single fibre lead; secondly, because light traverses the optical pathlength twice for a given physical cell length; and, thirdly, because the arrangement is, to a certain degree, self aligning. The alternative fibre=>lens=>lens=>fibre single-pass arrangement (where light from the fibre is collimated, passed through the cell, then re-focussed into a fibre at the far end) requires very careful alignment; firstly, of the fibre positions in the focal plane of the lenses; and, secondly, of relative angular orientations of the collimator and re-focussing optics units. The retro-reflective arrangement only needs simple care to correctly focus one collimator module (the same module as used to refocus returning light) and to ensure the collimated beam is directed at a point close to the centre of the retro-reflector. Under these conditions, the returning beam will strike the same lens and be correctly focussed back into the fibre lead.

Some results for measurement of  $\text{O}_2$  using this arrangement, are presented in Fig. 13. For these measurements, the curves presented show the measurement detector modulation index response (obtained by dividing the AC signal by the mean DC level) when alternatively filling the measurement cell with pure dry nitrogen and dry air (circa 20%  $\text{O}_2$ , 80%  $\text{N}_2$ ). In one instance, a single-pass scheme is used, while the other employed the double-pass retro-reflector arrangement. The doubling of the measurement signal modulation index is clearly

evident for the two-pass configuration, and the magnitude of both signals agrees well with that calculated in Sect. 3 (Fig. 9) to model this experiment. The transient responses in both sets of results are limited by cell filling times, as flow of gas into the cell and mixing/displacement to ensure full removal of the earlier gas fill has to take place. The true response time of the measurement system is set by the much shorter electronic integration time of the PC-based lock-in processor and filter used to recover the modulation index. The latter was typically set to a 10s time constant for these measurements.

### FIGURE 13

It can be seen that the method works well for this application, even though these represent very early measurements with our first bench set-up. Initial results suggest a noise-limited detection level below 1 % for O<sub>2</sub>, although we still need to improve the mechanical stability of our optical-bench arrangements to reduce environmental sensitivity. We are presently constructing more stable optical and mechanical arrangements for our measurements, and hope to report on enhanced results at a later time. As yet, crosstalk measurements to examine the undesirable influence of other likely gaseous contaminants have to be performed. However, we confidently expect the method to exhibit the excellent selectivity characteristic of correlation spectroscopy methods [12] when measuring gases with fine line absorption spectra.

#### 4. Conclusions

We have reported new results for gas detection using the CoSM scheme for correlation spectroscopy. This includes the simulated responses of the detection scheme for various concentrations of O<sub>2</sub>, CO, and CO<sub>2</sub>, using spectral data from the Hitran database, and also new experimental results for O<sub>2</sub> using low-cost LED sources. To our knowledge, this is the first such investigation for O<sub>2</sub> using LED sources with the highly-selective correlation approach.

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### **Biography**

**Prof John P. Dakin** is a Research Professor at Southampton University, supervising R & D in optical instrumentation, particularly optical fibre sensors. He was a BSc and PhD student at Southampton University and remained as a research fellow until 1973. He then spent 2 years in Germany at AEG Telefunken, 12 years at Plessey UK and 2 years with York plc, before returning to the University in 1990. He is the author of over 160 technical and scientific papers, and over 120 patent applications, and has edited or co-edited five books on optical fibre sensors. He was a visiting professor at Strathclyde University (UK). He is a frequent invited speaker and chair at major international conferences, and had the honour of being technical programme chair of the major OFS '89 Conference in Paris

Professor Dakin has won a number of awards, including "Inventor of the Year" for Plessey Electronic Systems Limited and Electronics Divisional Premium of the IEE. He has been responsible for a number of key electro-optic developments, including the sphere-lens optical fibre connector, the first WDM optical shaft encoder, the Raman optical fibre distributed temperature sensor, the first realisation of a fibre-optic interferometric hydrophone array sensor, the Sagnac loop disturbance location method and a number of novel optical gas sensing methods.

**Dr Mark J. Gunning** was born in Durban (South Africa) in 1971. He completed a PhD in Physics at the University of Natal in 1999, and has since filled the role of research fellow at the University of Southampton. His current research interest are devoted to optical fibre

sensing schemes, with specific interest in fibre grating and laser sensors as well as spectroscopic gas detection.

**Paul Chambers** was born in Belfast (N. Ireland) in 1979. He graduated with a first class honours B.Eng Degree in Electronic Engineering in 2001 at the University of Limerick, Ireland. In 2001, Paul started a PhD. course at the Optoelectronics Research Centre (ORC) at the University of Southampton, and involvement with this collaborative work forms part of his PhD research project studies.