THE BIG THREE - ON-LINE MONITORING OF GREEN HOUSE GASES

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ABSTRACT

National emissions regulations have historically targeted the common stack gas pollutants which have long been known to cause damage to health or ecology, but there is growing concern about the long term effects on the world's climate from what were hitherto less obvious pollutants. The Kyoto Protocol has identified six gaseous pollutants as "green house gases" and the top three in particular, carbon dioxide, methane and nitrous oxide have become subjects of some interest. Monitoring for emissions of these gases requires appropriate analyser hardware, and infrared techniques are the most relevant. Although various transducer designs suitable for measuring these components have existed for some time, recent advances in gas filter correlation techniques now provide sensitive and accurate measurements of nitrous oxide and methane with low residual cross-interferences. For the effective measurement of percent levels of carbon dioxide a new development in ultra-compact, solid-state, single beam IR techniques, utilising a pulsed source, is now able to provide this analysis in flue gas in a miniaturised, high performance and cost-effective package.

1.   INTRODUCTION

Environmental regulations defining limits for the emissions of industrial pollutants to the atmosphere have long been in place in most nations, and historically these have targeted those acidic or toxic pollutants associated with causing direct damage to ecology or health, for example via acid rain or ground level ozone formation. Such regulations have contributed to the growing pressure for firm environmental measures world-wide, which in turn have created a major global business in the supply of environmental products and services, forecast to grow at substantial rates over the next few years [1]. As part of the overall environmental business, the market for continuous emissions monitoring systems (CEMS) for the usual gaseous pollutants has seen fairly constant growth, with increasing requirements for more sensitive measurements at lower concentration levels. More recently, since the identification of the global warming issue and the establishment of the United Nations Framework Convention on Climate Change (UNFCCC), further gases have begun to attract particular attention from the international community, the most notable being carbon dioxide (CO_2), the primary "green house gas" (GHG), held responsible as a major cause of global warming. The 1997 Kyoto Protocol (the result of COP-3 - the third Conference Of Parties to the UNFCCC, held in Japan) identified this and five further gases as critical GHGs whose emissions to atmosphere must be reduced in order to reverse the global warming trend, and consequently started the process of international negotiations on reduction targets. Within the European Union (EU) this has recently resulted in major CO_2 emissions reduction targets being agreed by member states, to be achieved by 2008-2012. Countries committed to big reductions include Germany (21% reduction from 1990 levels), the UK (12.5% reduction) and Italy (6.5% reduction). In addition, EU member states are now required to submit annual reports on their progress in meeting their targets for GHG emissions reductions [2].

The second most important GHGs were identified as methane (CH_4) and nitrous oxide (N_2O). Whereas the major cause of anthropogenic CO_2 emissions is combustion, the two biggest sources being power generation and road transport, the sources of CH_4 and N_2O are various. In the UK it is estimated [3][4] that of the total 1996 CH_4 emissions (78 million tonnes as CO_2 equivalent), 46% came from landfill sites, 25% came from bovine agriculture, 10% from natural gas grid leakage and 9% came from coal mines. In contrast, the UK's N_2O emissions during that year amounted to 58.6 million tonnes (as CO_2 equivalent) and were believed to arise mainly from arable agriculture (49%), nitric acid and adipic acid process plants (37%) and road transport (5%). For comparison, the UK's CO_2 emissions for the same year amounted to 593 million tonnes, calculated to be about 2% of the global total.

The top three GHGs in particular (CO_2, CH_4 and N_2O) have therefore become the subject of interest, especially in emissions from combustion processes and in gases produced by landfill sites or certain chemical processes. Each of them, by virtue of the fact that they are GHGs, have strong infrared (IR) absorbances and hence are entirely amenable to instrumental analysis by IR means. The IR technology appropriate for their analysis is clearly

dependant on the measurement sensivity required, however in addition to sensitivity there are many other measurement parameters which should be considered as necessary for ensuring not only high performance but also reliable practical operation. The increasing recognition of the need for detailed assessment of various parameters for CEMS analysers in particular has resulted, for example, in the recent UK MCERTS certification scheme performance standards [5] which are a valuable yardstick by which to evaluate the selected measurement technology.

In the case of CH_4 and N_2O their emissions, from whatever source, are generally at trace levels and a high sensitivity technique is needed when monitoring is considered. IR gas filter correlation (GFC) techniques have become very well accepted for monitoring trace level pollutants in flue gases, giving the advantages of high sensitivity and low residual cross-interferences. Both CH_4 and N_2O have a sufficient degree of rotational fine structure in their IR absorbances to enable the application of GFC techniques, and this paper reports recent developments in GFC transducer technology to produce high performance measurements of these two gases.

The quantification of high volume percent levels of carbon dioxide in flue gas is inherently less arduous, but nevertheless requires an appropriate form of technology to be applied to achieve it in an accurate, yet cost-effective, way. The recent development of a simple, single beam IR transducer with no moving parts, using a novel pulsed IR source, now enables such performance to be achieved. This paper will also discuss the principles of this IR technology, and the factors governing the achievement of high measurement performance, low cross-interferences, reliability and compact size.

2   GAS FILTER CORRELATION DEVELOPMENTS

A full treatment of the principles and history of GFC techniques has been previously presented [6].and a brief review only of the principles is given here.

Taking the example of a nitric oxide (NO) flue gas measurement, broad band IR radiation from a hot element source passes alternately through one of two gas filters mounted on a chopper wheel (Fig. 1). One contains nitrogen and the other contains the target gas of interest, in this example NO. When the nitrogen gas filter is in position, no absorption takes place. When the NO gas filter is in position, absorption takes place reducing the IR intensity in the beam at the characteristic wavelengths for NO.
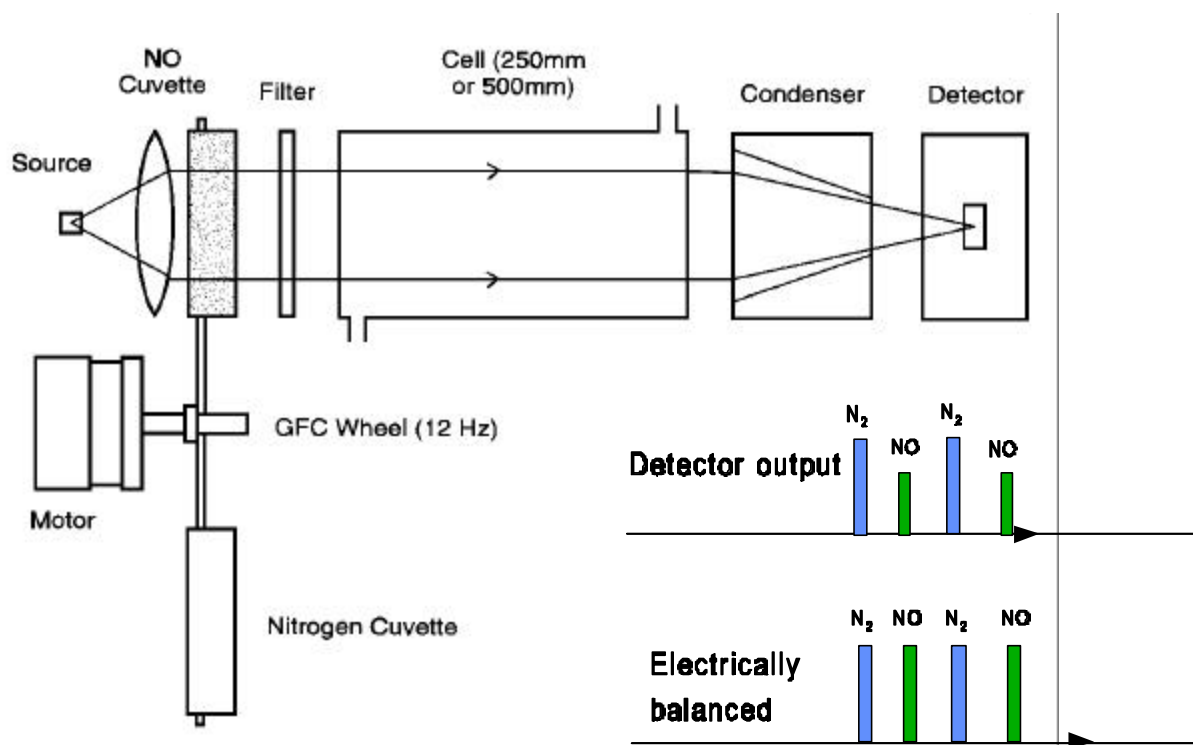

Figure 1   Schematic of the Servomex Gfx1210 series gas filter correlation transducer, showing the detector output before and after electronic zero adjustment with nitrogen in the sample cell.

The temporally spaced beams then pass through a narrow band pass filter which limits the IR region to a specific part of the absorption spectrum and then into the sample cell. When radiation that has passed through the nitrogen gas filter passes through a gas sample containing NO in the sample cell, absorption occurs according to Beer's law and produces a reduction in this "nitrogen" detector signal. This signal is effectively a measurement signal.

In contrast, radiation that has passed through the NO gas filter has had the intensity at the characteristic NO wavelengths already significantly reduced, and so any further absorption in the sample cell is small, resulting in a fairly constant "target gas" signal. However that energy which is transmitted makes an excellent reference signal as it has exactly the same spectral distribution as the "nitrogen" signal. Therefore the resulting "nitrogen" and "target gas" detector signals are effectively measure and reference signals, and they are electronically balanced out under zero gas conditions (e.g. with nitrogen in the sample cell) to set the zero output. Thereafter, calibration and linearisation provide the necessary mapping to experimentally measured values to give a high performance, high sensitivity NO concentration measurement from the transducer.

In principle, GFC techniques are inherently resistant to the effects of cross-interfering gases present in the sample, since the transducer is effectively characterised to the extremely fine IR absorption fingerprint of the gas hermetically sealed in the target gas cuvette. In effect a background gas with an absorption in the same region as that of the measurement gas may only interfere if there is exact overlap with this fine structure of the target gas. This immediately reduces the likelihood of any interferences. Furthermore by careful selection of the IR interference filter parameters to exclude regions where overlap with other gases is possible, very low cross sensitivity can be achieved. Where some degree of overlap is unavoidable an alternative method of minimising cross sensitivity is to utilise a zero crossing point for cross sensitivity with respect to centre wavelength (CWL) of the IR filter. In the NO example, there are a large number of water vapour lines across the 5.3 μm region where NO has it absorption. Some of these moisture lines overlap the NO lines exactly, giving a positive cross sensitivity and some fall exactly between the NO lines giving a negative sensitivity to water vapour. As the CWL of the IR filter is shifted in wavelength, the cross sensitivity falls to zero where the contributions from overlapping and non-overlapping lines cancel, resulting in very high selectivity to NO alone.

2.1   MEASUREMENT OF NITROUS OXIDE

An excellent review of the sources of N_2O, including stationary combustion sources, and the various techniques available for analysis of N_2O has been prepared by the UK Environment Agency [7]. As a strong IR absorber with a good degree of rotational fine structure N_2O is an ideal compound for the application of GFC measurement techniques. However, like the traditional flue gas pollutants it too frequently coexists with large amounts of water and CO_2 in combustion stack gases, or potentially with other nitrogen oxides in stack gases from processes involving nitric acid. The instrument design must therefore ensure that cross-interferences from such compounds are minimised. In reality, the IR absorbances of both NO and NO_2 (nitrogen dioxide) are sufficiently distant from the main N_2O band at 4.5μm not be have any significant effects, but the presence of water vapour, large amounts of CO_2 plus some traces of CO are all potential problems since they each have IR absorbances which do overlap the N_2O absorption to one degree or another (Fig. 2). This means that a combination of measures must be taken to produce an acceptable instrument performance.

Optimising the IR filter parameters for minimum CO cross sensitivity and minimum moisture cross sensitivity is the first vital step, however this does not in itself give sufficient resistance to the interfering effects from CO_2. A different approach must be adopted to deal with this, and one approach is to remove the CO_2 characteristic wavelengths from both measure and reference beams completely by placing a static gas filter in the beam containing a high concentration of CO_2. Alternatively, the measure gas filter can be filled with CO_2 and the balance of the reference gas filter can be CO_2. This is the more practical approach and results in good cross sensitivity rejection to all of the interferents. The typical performance achieved is <0.5vpm N_2O residual interference for either of 500vpm CO_2, 10vpm CO or 2% water vapour for an instrument measuring 0-50vpm N_2O minimum range. At the highest levels of interfering components in typical CEM applications even 20% CO_2 gives only +3.5vpm N_2O and 100vpm CO gives -3.5vpm N_2O, and hence the overall interference effects are minimal.
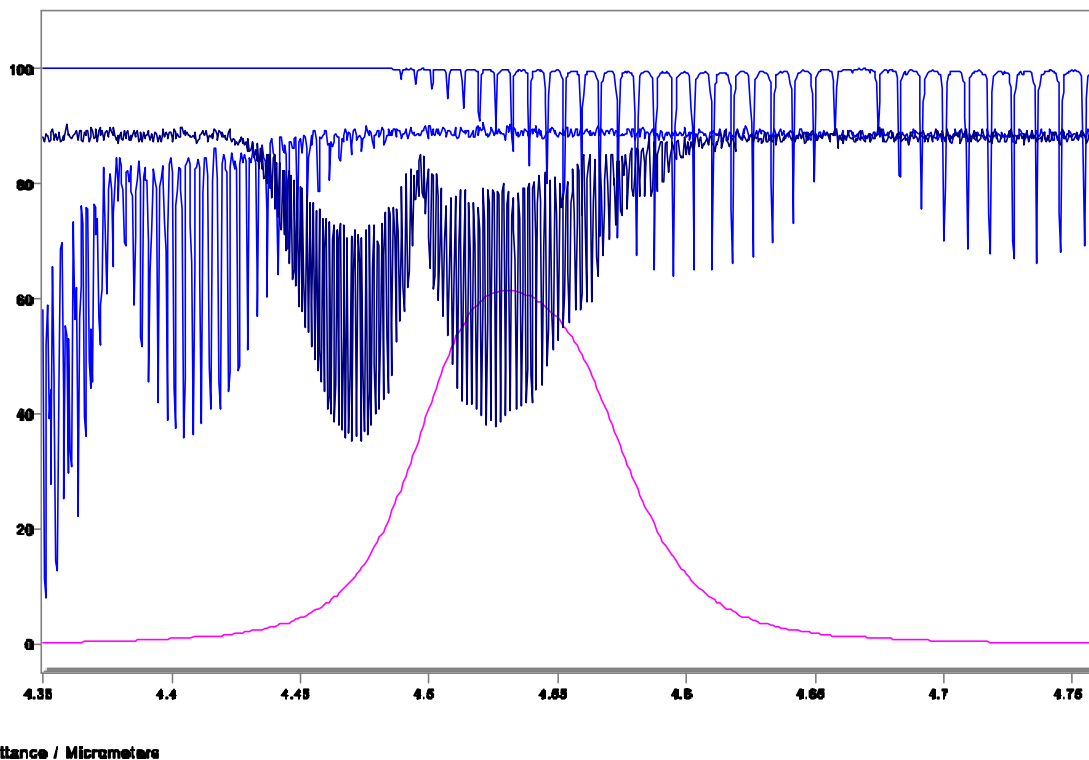
Figure 2   The spectra of CO_2 (left), CO (top and right), N_2O (centre) and a typical IR filter (bottom) used for the GFC measurement of trace N_2O.
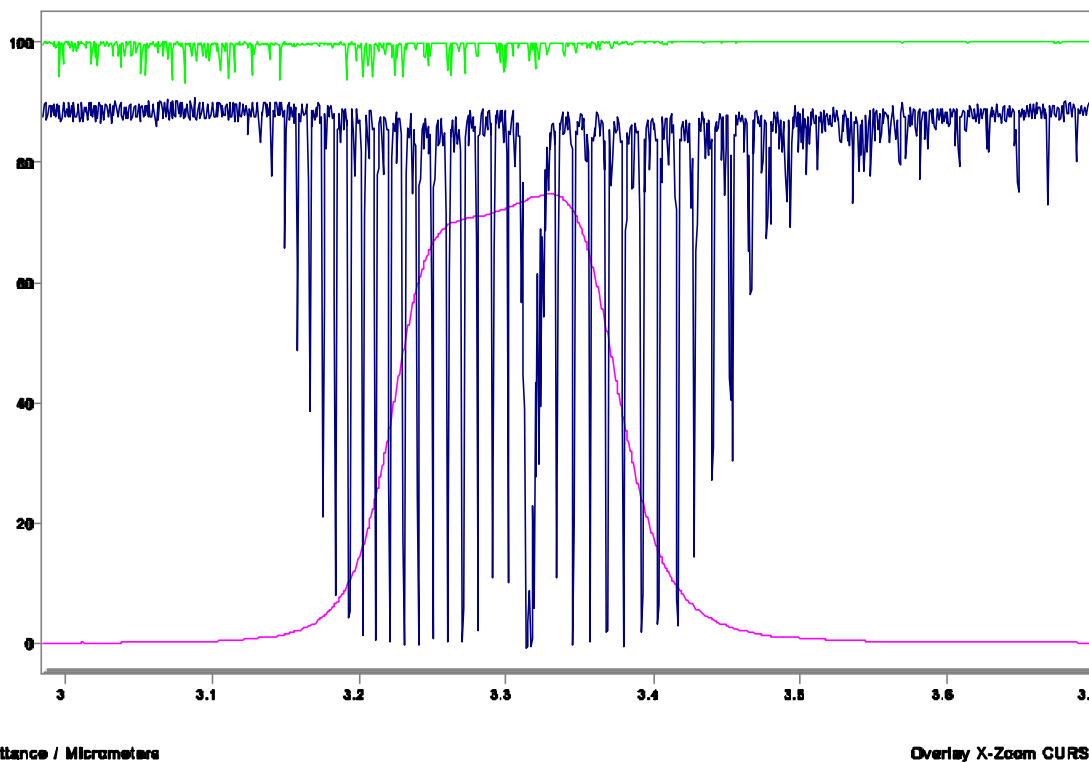
Figure 3   The spectra of CH_4 (centre), a typical IR bandpass filter (bottom), and water vapour (1%v/v.m) (top).

2.2   MEASUREMENT OF METHANE

Methane (CH_4) is inherently a fairly weak absorber although with a lot of fine structure, again an ideal candidate for GFC analysis. As previously noted UK emissions of methane are predominantly from landfill sites, with lesser quantities from sources such as coal mines. This means that where measurements are required there are unlikely to be significant quantities of the other traditional pollutants in the sample, but every likelihood of significant quantities of moisture and CO_2. On some landfill site traces of H_2S may also be present. Fortunately CH_4 has a major absorbance around 3.3μm, well away from the absorbances of the other components mentioned, although this region does have some moisture bands. Therefore the need to realise efficient rejection of cross interferences can be largely traded off against optimising the basic CH_4 measurement sensitivity.

By filling the reference gas (CH_4) filter to a pressure and optical density equal to or greater than that expected for CH_4 in the sample cell, the line widths and intensities of the IR absorption can be increased so as to maximise the degree of correlation, or overlap, between the spectra of sample gas and the gas filter. The IR bandpass filter parameters are also optimised for maximum sensitivity whilst maintaining a reasonably low figure for moisture cross sensitivity (Fig. 3). This results in a typical minimum measurement range of 0-50vpm CH_4 with cross sensitivities of only +2.5vpm CH_4 for 2% water vapour, and only +1vpm CH_4 for 10% CO_2.

It should be noted that the cross sensitivity to other light hydrocarbons is expectedly larger, due to the operation at the common C-H stretch wavelength. However they are still fairly small, for example 2000vpm propane gives a reading of +50vpm CH_4. and unlikely to be a significant issue in typical methane monitoring applications.

3   IR TRANSDUCERS FOR HIGHER CONCENTRATION CARBON DIOXIDE MEASUREMENTS

The quantification of substantial volume percent levels of carbon dioxide in flue gas is inherently less arduous since not only is the concentration much higher than that of the other typical measurands but also CO_2 itself has a particularly strong and specific IR absorbance at 4.2μm. This means that a simpler, more compact form of transducer technology can be applied to achieve the CO_2 measurement in an accurate, yet cost-effective, way. The development of a such a solid-state, single beam IR transducer with no moving parts, using a novel pulsed IR source to obtain the necessary signal modulation, now enables the required performance to be achieved in a very compact and cost-effective design.

The Ir1520 transducer is a single beam, single wavelength design and has three basic components. Firstly a patented [8], sealed infrared source unit which produces a pulsed beam without the use of any moving parts. This also incorporates an IR bandpass filter selected for the measurement required. This assembly is attached to a miniaturised sample cell though which the gas sample constantly flows. Finally there is a solid state detector module utilising a pyroelectric detector chip. Special attention is paid to insulation and temperature control in the transducer to ensure stability with respect to ambient temperature changes. In addition, all optical "dead spaces" are eliminated in the design. A "housekeeping" electronics circuit board, which can also accommodate calibration and linearisation functions, completes the assembly. This design can be adapted to provide a family of transducers suitable not only for CO_2 measurements over a wide selection of ranges (0-2500 vpm up to 0-100%), but also suitable for some percent level measurement ranges of CH_4 or CO.

The source is shown in Figure 4 and comprises of a specially oxidized nichrome element suspended between spring supports and located above a concave reflector. The element is heated with a pulsed signal to provide an efficient means of providing a pulsed infrared beam of constant average intensity and long life. Lifetime tests in which the source was over-powered have shown that the expected life under normal operation is in excess of 3 years. The pulsed infrared radiation then passes through a carefully specified, integrated narrow band pass IR filter to provide energy corresponding to the main absorption band of CO_2.

This energy then passes through the sample cell and is absorbed according to Beers Law. The sample cell is fitted with sapphire windows sealed with 'o' rings which provide gas tight sealing and alignment for the source and detector sections at either end. Sample cells of between 1mm and 160mm in length are used, depending on the gas and range, giving an internal volume of between 10 and 120μl. This very small sample volume allows fast time responses to be achieved. For example the 10μl cell gives a response time T(10-90) <4s using a sample flow rate of 200ml/min.
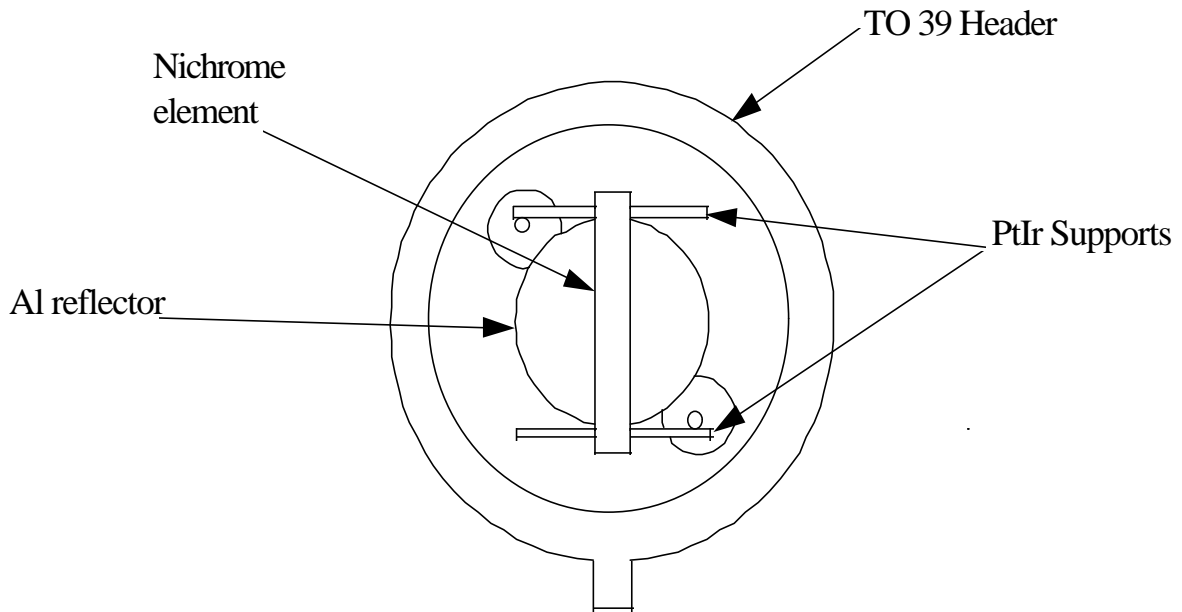
Figure 4   Novel pulsed IR source design

The remaining energy not absorbed in the sample cell falls on the active area of a pyroelectric detector which provides an electrical output proportional to the rate of change of incident energy pulses. This pulsed beam provides the necessary modulation of energy to allow the use of rate detecting low cost pyroelectric detectors. The detector unit is a fully sealed temperature controlled assembly with an integral preamplifier. The long pathlength cell variants also include a second heater and thermistor for the cell. This all helps to ensure a stable output independent of ambient temperature fluctuations.
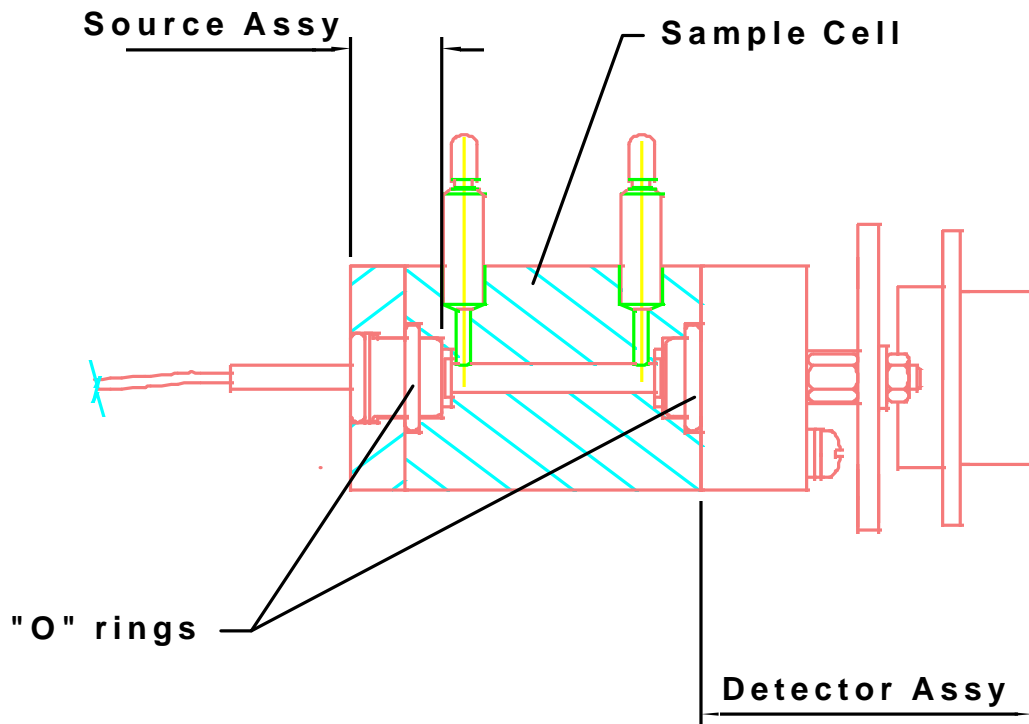

Figure 5   The Ir1520 infrared transducer in section, showing the source, sample cell and detector assemblies

As noted above the source, sample cell and detector are close coupled with no intervening dead spaces as shown in Figure 5. This eliminates the opportunity for dead volumes to become contaminated with atmospheric moisture and CO_2, which could contribute to drift and decreases in sensitivity. This arrangement also maximises optical throughput without the necessity of any refractive optics.

The signal conditioning electronics takes the amplitude modulated signal from the preamplifier detector signal and demodulates the carrier by a full wave synchronous detector arrangement to give a positive output equal to the mean value of the original input carrier signal. This signal is then passed through a scaling amplifier, through a lineariser to the final output stage to produce a DC output proportional to the concentration of gas in the sample cell to an accuracy of 1% of measuring range. Either an integrated analogue lineariser can be used to provide a linear output signal from the "housekeeping" board, or the unlinearised measurement can be output and a digital linearisation algorithm used when the transducer is mounted in a standard microprocessor-controlled CEMS analyser.

These transducers are now becoming integrated into standard CEMS analysers and are able to provide a highly cost-effective and reliable solution to CO_2 measurement requirements, particularly considering that they can be used in combination with other GFC or paramagnetic oxygen measuring transducers in the same analyser chassis. In the Xentra 4900 design transducers for % CO_2, % oxygen and trace CO, for example, can be mounted in one analysers to provide the three measurements simultaneously on one sample stream.

4   CONCLUSION

The GFC technique is particularly suited to make measurements of trace levels of GHGs since these materials are, by definition, strong IR absorbers and also have good fine structure in their absorbances. The extension of this technique to monitor trace methane and nitrous oxide therefore results in measurement transducers with high sensitivity and good specificity. In contrast, monitoring the comparatively high levels of carbon dioxide in flue gases can be accurately achieved with an extremely compact IR sensor, and the recent development of a single beam, single wavelength miniaturised transducer utilising a pulsed source and temperature control offers a very robust solution to this measurement requirement. Finally, the effective miniaturisation of these sensors not only saves mounting space in the analyser, since several transducers can be mounted in one 3U 19" rack analyser package, but also helps to contain instrument costs.

REFERENCES

1   'Global Environmental Markets: An Update', JEMU/DTI, DTI Export Publications, London, 1997, ISBN 0 85605 3570

2   'International Environment Reporter', Bureau of National Affairs, Washington, 1999, 22 (10), 391

3   'Digest of Environmental Statistics No.20 1998', DETR, HMSO, London, 1998
         (also at: www.environment.detr.gov.uk/des20/index.htm).

4   'The Environment in your Pocket', DETR, London, 1998, 98EP0190, 14-15

5   'MCERTS Performance Standards for Continuous Emissions Monitoring Systems', Environment Agency, London, 1998

6   'Gas Filter Correlation Techniques applied to CEMS Analysers', Bruce S.H., Middleton P., in proceedings of the CEM'98 Conference, NPL, London, 22nd.-24th. April 1998

7   'A Review of the Sources and Monitoring of Nitrous Oxide', Environment Agency National Centre for Compliance Assessment, Research Report HMIP/CPR2/41/1/59, 1998

8   US Pat. 5324951, Eur. Pat. 0549634