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GB 2595936 B

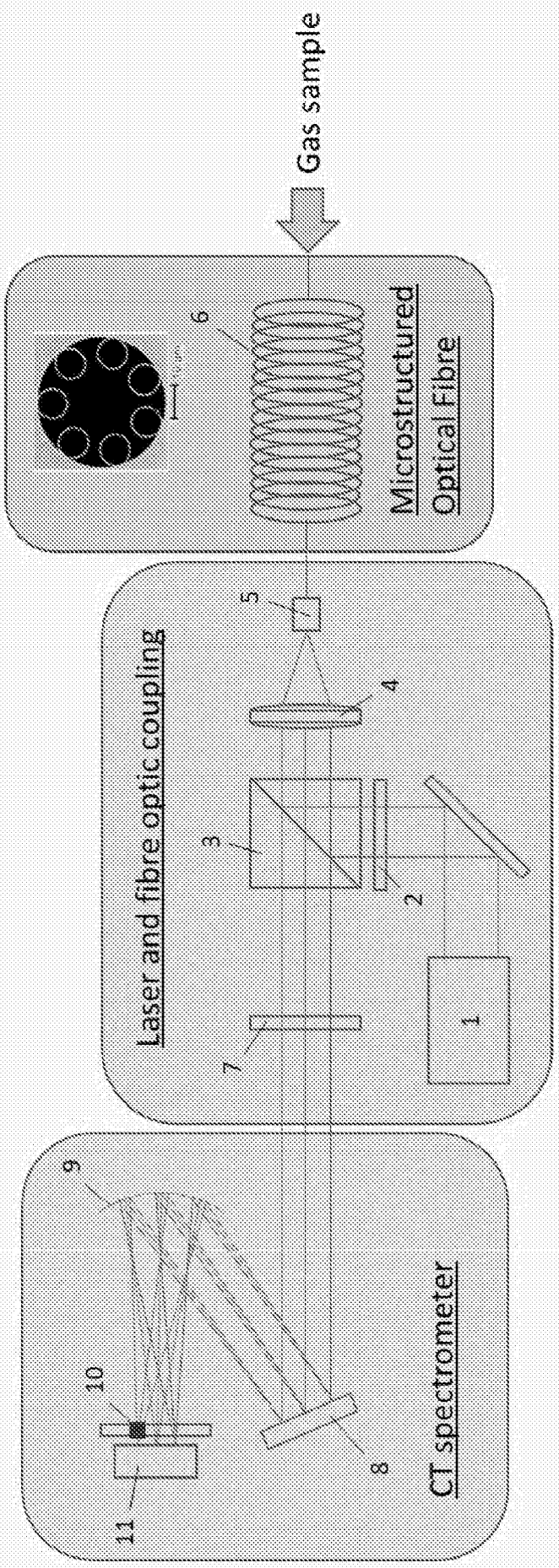
Gas sample
Microstructured
Optical Fibre
Laser and fibre optic coupling
CT spectrometer
1
2
3
4
5
6
7
8
9
10
11

FIGURE 1

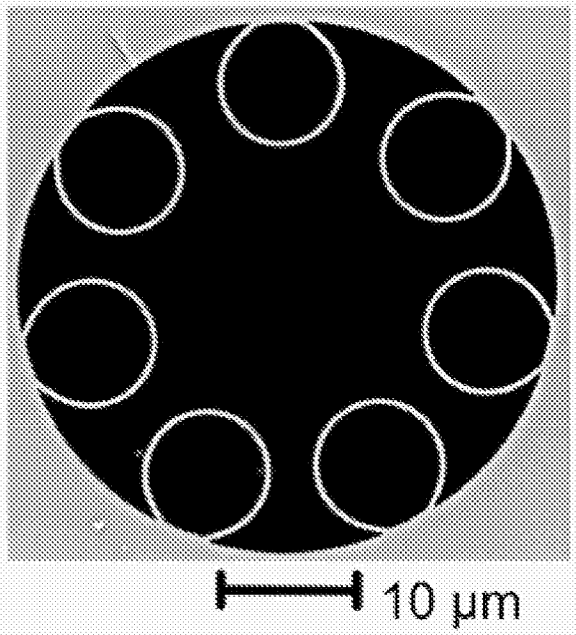

FIGURE 2A

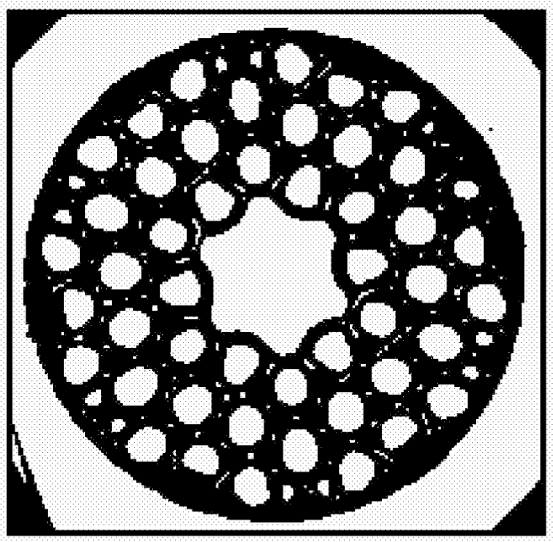

FIGURE 2B

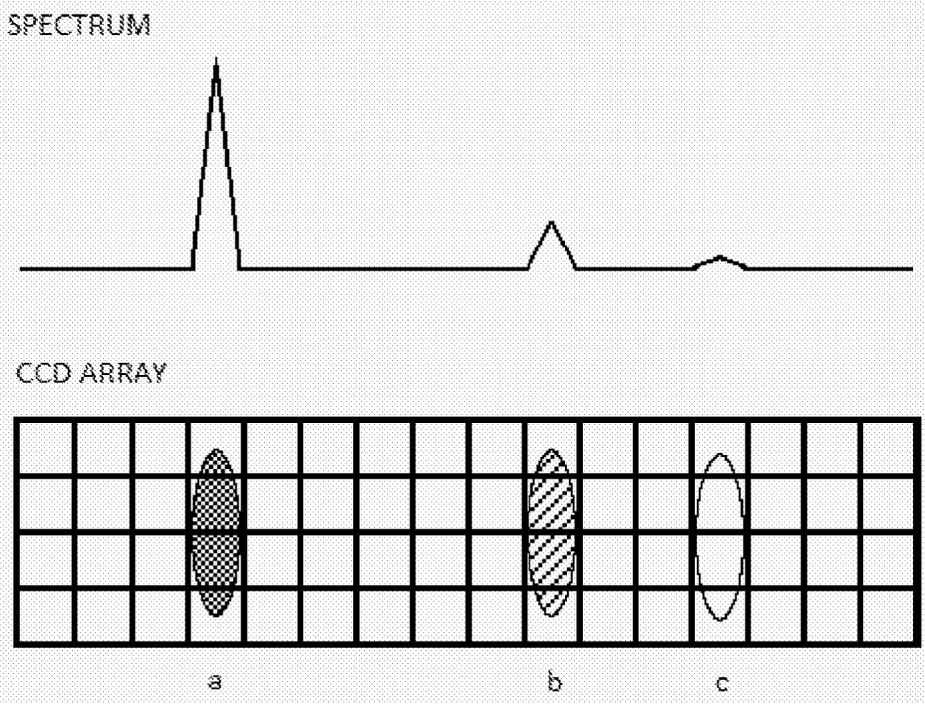

FIGURE 3A

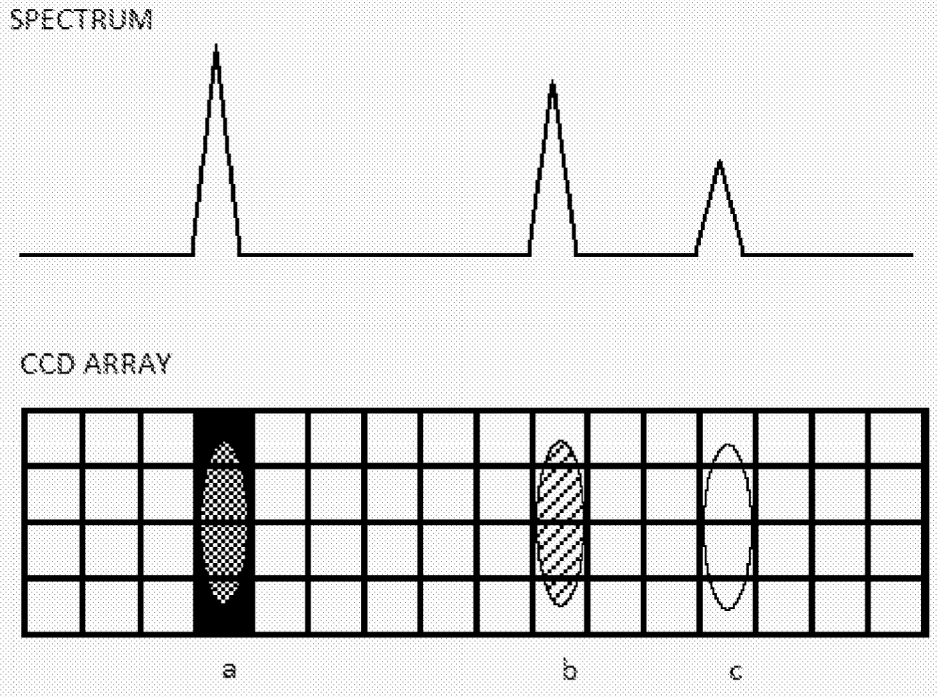

FIGURE 3B

GAS PHASE RAMAN INSTRUMENT FOR THE DETECTION OF GASEOUS SPECIES USING A HOLLOW CORE FIBRE

The present invention relates to apparatus and methods providing improved sensitivity in gas phase Raman spectroscopy using a hollow-core optical fibre.

Raman spectroscopy is a powerful tool for identification and quantification of unknown substances. All molecules provide a unique spectral fingerprint that can be measured. This has led to a variety of instruments being developed that observe solid and liquid samples.

Making Raman observations of gases is a significant challenge due to the small scattering cross section of gaseous molecules. This is particularly true for samples from gas pipelines, where a significant number of species can be present at various concentrations. Observations of gases at concentration of below 3% and down to parts-per-billion (ppb) levels are beyond the capability of current systems.

The strength of the Raman signal is given by:

$$S = \frac{L_P I_E A \alpha \Delta R e^{-2\tau}}{\pi R^2},$$

where L_p is the laser power, I_E is the instrument efficiency, A is the telescope of the collection aperture, ΔR is the depth of the sample being measured, R is the distance to the target, α is the scattering cross section and τ the attenuation of the media. Therefore, if the path-length of the interaction between the laser and the gas species can be increased, the Raman signal will be stronger. A stronger Raman signal will improve the sensitivity of a gas phase Raman instrument for the detection of gaseous species.

One method to increase the path-length is the use of hollow core micro-structured optical fibres (HC-MOFs). HC-MOFs are a special kind of optical fibre which confine light inside a hollow core surrounded by a micro-structured cladding. US 7,595,882 describes hollow-core waveguide-based Raman systems and methods using a hollow core photonic crystal fibre (HC PCF) but suggests that any hollow-core, wave-guiding device that exhibits a low attenuation at the operating optical frequencies would be suitable. An earlier example can be found in US 2006/0251369.

HC-MOFs have holes in their cross-sections to confine light in the fibre core, this itself consists of a hollow region that runs along the entire fibre length. By filling the fibre core with a sample gas, the gas-laser interaction pathlength can be significantly increased to produce a strong Raman signal.

Furthermore, the only alignment requirement within the system is that of the fibre to the excitation source (and the Raman signal generated within the fibre to the spectrometer). This contrasts with competing spectroscopy techniques (such as cavity enhanced spectroscopy or cavity ring down methods). Thus, the system can be made inherently robust.

Multiple fibre designs can be used, including the tubular Hollow Core Anti-Resonant Fibre (HC-ARFs) and the Kagome HC-ARF.

However, the improved sensitivity achieved using a HC-MOF results in a significant problem associated with instrument dynamic range. The limited dynamic range of the detector can restrict the number of species that can be simultaneously observed, reducing the instrument specificity. Specificity is one of the main advantages of using Raman spectroscopy in analysing samples.

For example, in natural gas samples, the gas species being examined can have very low concentrations (< 1ppm). These target gas species will typically be within a sample which may consist of >95 % methane. The limited dynamic range of the detector restricts the ability of the device to make observations of multiple target gases of different concentrations. Furthermore, it is often required that multiple target species are measured simultaneously.

The apparatus and method described herein overcomes problems with the prior art and allows the analysis of a gas sample containing multiple target species with widely varying concentrations. Furthermore, the target species can be analysed simultaneously.

The apparatus for analysing gas samples comprises: a monochromatic or near monochromatic light source; a hollow core micro-structured optical fibre, HC-MOF, in optical communication with the light source, the HC-MOF containing a gas sample to be analysed;

and a detector in optical communication with the fibre for detecting a Raman signal from the gas sample, wherein a mask is mounted between the fibre and the detector to attenuate one or more selected frequencies of the Raman signal.

Preferably, the one or more selected frequencies correspond to one or more peaks or expected peaks in a Raman spectrum of one or more components of the gas sample that are present or are expected to be present in high concentration.

In one embodiment, the attenuating mask blocks the selected frequencies of the Raman signal.

The mask may comprise a variable filter which is dynamically controllable.

Preferably, the detector comprises a plurality of detector pixels each detecting a specific frequency of the Raman signal; and the mask attenuates the light reaching one or more selected pixels of the detector.

In one embodiment, the gas may be natural gas and the selected frequencies may correspond to the Raman spectrum of methane.

Preferably, the HC-MOF has a tubular design. It may have one or more laterally located apertures to allow the gas sample to flow into or out of the core. The gas inside the HC-MOF may have a differential pressure along the HC-MOF to generate a longitudinal gas flow in the HC-MOF core. The HC-MOF may be uncoiled.

In one embodiment, the light source, HC-MOF, mask and detector are mounted in a portable unit.

In one embodiment, the apparatus may comprise a plurality of HC-MOFs. These may be connected to the same detector.

A method for analysing multiple gas samples comprises: filling the core of a hollow core micro-structured optical fibre with a gas sample; exciting the gas using a monochromatic or near monochromatic light source to generate a Raman signal; filtering the signal to

attenuate one or more selected frequencies in the Raman signal; and using the filtered signal to identify one or more low concentration components of the gas sample.

The invention will now be described solely by way of example and with reference to the accompanying drawings in which:

Figure 1 shows a schematic diagram of apparatus for analysing a gas sample according to one embodiment of the present invention;
Figure 2A shows, in cross section, an example of a tubular fibre design which may be used in the present invention.
Figure 2B shows, in cross section, an example of a Kagome fibre design, which may be used with the present invention;
Figure 3 shows the effect of the present invention on a Raman spectrum. Figure 3A shows a detector and an exemplary spectrum produced without using the present invention. Figure 3B shows a detector and exemplary spectrum (for the same sample) in accordance with an embodiment of the present invention.

Figure 1 shows an apparatus for analysing gas samples, according to one embodiment of the present invention. The apparatus comprises a Raman excitation source 1, a hollow-core micro-structured optical fibre 6, and a detector 11. A dichroic filter 3 is positioned to direct excitation light from the excitation source 1, via a laser line filter 2, an aspheric lens 4 and fibre coupling mechanism 5 towards the fibre 6. The dichroic filter 3 also directs the back-scattered Raman signal from a sample in the fibre 6 to the detector 11 via a long pass filter 7 which removes the excitation light from the signal. The Raman signal is dispersed via a diffraction grating 8 and focused via a mirror 9 onto the detector 11. A mask 10 for attenuating one or more selected frequencies of the Raman signal is positioned in an optical path between the grating 8 and the detector 11. The mask may be positioned inside a spectrometer.

In the embodiment shown, the Raman signal is free space coupled to the detector 11. Additional optical elements, such as lenses and mirrors, are used to focus and collimate the excitation light and the Raman signal. In particular, aspheric lens 4 both focusses the excitation light into the HC-MOF 6 and collimates the received Raman light.

In an alternative embodiment, a multimode fibre (not shown) directs the Raman signal to the spectrometer assembly: the grating 8, the focussing mirror 9 and the detector 11. This optional feature facilitates the coupling and uncoupling of the spectrometer assembly.

The HC-MOF 6 is tubular in design. The fibre length can be tailored to specific applications. In one embodiment, the fibre is 20m long. A gas sample to be analysed is contained in the core of fibre 6. In a preferred embodiment, the target gas sample may be from a natural gas pipeline. The gas may be held at high pressure to increase the density of the gas molecules and strengthen the Raman signal. The pressure may be up to 120 bar without damaging the fibre.

The fibre 6 may have one or more laterally located apertures (not shown) to allow a gas sample to flow into or out of the fibre core. Alternatively, gas may be introduced at one end or both ends of the fibre 6. Alternatively, gas may be introduced at one end of the fibre 6 and withdrawn at another end of the fibre 6. This can provide a differential gas pressure along the fibre to generate a longitudinal flow in the fibre core. This allows continuous monitoring of a gas supply which may be changing in composition over time. In particular, the apparatus can detect very low levels of impurities in the gas flow.

The HC-MOF may be one of several different designs and may guide light within the hollow core by either photonic bandgap or anti-resonant guidance (or even a combination of both). These designs may include hollow core tubular, Kagome, nested anti-resonant nodeless fibres (NANF) or hollow core photonic bandgap fibres (HC-PBF).

In Figure 2A, a tubular design fibre is shown. To give an indication of size a scale bar is shown. The lighter areas are silica and the black areas are air. These sizes can vary as the fibre design is tuned to a specific transmission window. Alternative fibre designs may be used, such as a Kagome design shown in Figure 2B which can provide a higher transmission bandwidth allowing a greater spectral range to be examined. The fibre has a hollow core to contain the gas sample to be analysed and is designed to guide light in the hollow core along the fibre. The fibre may be a photonic band-gap fibre optimised to guide the frequencies of the excitation light and the Raman signal.

In one embodiment, a plurality of fibres can be used to simultaneously monitor several gas source locations. The locations may be distributed across a large site. The excitation light path can be divided into multiple excitation paths, each being directed to a different fibre simultaneously, or the excitation light path may be switched between different fibres as required. The Raman return signal paths can be optically combined and directed to a single detector. Only one detector is required as the fibre or fibres being analysed are selected by activation of the excitation light path(s).

Using this approach multiple fibres could be used to study the same sample, effectively increasing the gas filling area. This would speed up the time required to fill the fibre and integrate a given sample, allowing faster analysis.

In a preferred embodiment the light source 1 is a laser but it may be any monochromatic or near monochromatic light source capable of generating light which can interact with a gas sample to generate a Raman signal. In one embodiment, the light has a wavelength of less than 1000 nm, and greater than 200 nm. In one embodiment, the wavelength is 532nm.

A dispersive spectrometer may be used to detect the Raman signal but alternative instruments could be used. As shown in Figure 3, the detector comprises a plurality of pixels, each configured to receive a specific frequency of the Raman response. The pixels may be arranged as an array of pixels. The detector may be a charge coupled device (CCD) detector. The position of a pixel in the array may determine which frequency of the Raman response it detects.

Figure 3 provides an idealised example where the Raman signal comprises three frequencies (a), (b) and (c), each of which falls on a different column of pixels in the detector array. As shown in the corresponding Raman spectrum in Figure 3A, frequency (a) gives a much stronger signal than either frequency (b) or(c). It is therefore difficult to identify the spectral peaks produced at (b) and (c) in the spectrum.

In Figure 3B, a translucent attenuating mask is applied to the detector pixels corresponding to frequency (a). As shown, this reduces (as, in this example, the mask is not opaque) but does not eliminate the peak at frequency (a) in the spectrum. Importantly, the detector is not overwhelmed by the signal at frequency (a) and more photons can be detected at

frequencies (b) and (c) via increased integration times. This increases the dynamic range of the detector across a range of frequencies, by effectively reducing the photon counts of target frequencies, thereby effectively increasing the relative peak heights of other weaker Raman peaks.

The mask 10 is positioned to cover one or more specific pixels of the detector. Conveniently, the mask may be applied inside a spectrometer or it may be located elsewhere in the optical path followed by the Raman signal. The mask 10 may be an attenuating mask to reduce the signal reaching individual selected pixels of the detector 11 or an opaque mask to prevent any light reaching individual selected pixels. One or more pixels may be selected. The pixels that are selected for masking correspond to the Raman signal from strong scattering components of the gas sample. Mask locations are selected by identifying the main Raman lines from the target gas, for example the lines for methane in a natural gas sample. The detector is then carefully calibrated to pinpoint the exact pixels on which the light will fall and these pixels are selected for masking.

The mask 10 may be constructed of optically filtering media to either fully obscure or partially transmit the Raman signal over a particular region of the detector. If some of the signal is to be transmitted, this filtering media could be a neutral density filter (either absorptive or reflective) or interference filter. If the full signal is to be rejected over a given area, this can be achieved by using mirrors, for example d-mirrors can 'cut' the beam very accurately, or by knife-edged solid masks.

The mask 10 may be constructed by applying thin film dielectric or metallic coatings to one or more areas of a window on top of the spectrometer detector's sensitive area. These coatings will reject a known amount of light in particular areas on the detectors surface, equivalent to filtering given spectral ranges of the spectrometer. In another embodiment, the window is constructed of different materials, with the masked areas being provided by using materials with lowered or no transmission at the wavelength in question.

In another embodiment of the system the mask 10 could be constructed from dynamically adjustable materials, such a liquid crystal elements, allowing the amount of attenuation to be changed according to the application. Dynamic adjustment is particularly useful when

analysing a continuously variable gas flow where the concentration of the gas varies over time.

The location of the masked areas may be identified by simulation of the system to identify the expected peaks in the Raman signal and the corresponding pixels in the detector.

It can be difficult to ensure that the excitation light is accurately directed to the sample in the core of the HC-MOF 6. Accordingly, in one embodiment an alignment mechanism is used to couple the excitation light into the fibre 6. The alignment mechanism can move the lens 4 relative to the fibre 6 in very small steps in order to provide accurate alignment. The alignment mechanism may use piezoelectric actuators for fine adjustment. This also allows dynamic control, if required.

In one embodiment the alignment is achieved by optimising the signal recovered on the spectrometer detector. Alternatively, alignment may be achieved by maximising the signal detected by a power meter placed at the distal end of the fibre, such that the highest possible signal is achieved.

In an alternative embodiment the system may be mounted with an imaging camera that monitors the light entering the fibre to provide the position and focus of the laser at the fibre input.

In use, the excitation light emitted by excitation source 1 is reflected by dichroic filter 3 towards lens 4 which focusses the light into the centre of the HC-MOF 6. The light interacts with the target gas sample within the fibre 6 and generates a Raman signal. The increased path length provided by the fibre 6 improves the strength of all frequencies of the back-scattered Raman return signal.

The backscattered light from the fibre 6 is the then returned via the focussing lens 4 and the Raman shifted broadband light is transmitted through the dichroic filter 3. The broadband light is filtered by long pass filter 7 to remove the excitation signal and free-space coupled to dispersive spectrometer.

Attenuating mask 10 is located at specific pixels on the detector, where the Raman signal from the high concentration gas falls (e.g. methane in a natural gas sample). This reduces the signal at these locations, improving the dynamic range of the instrument and allows observations of other gasses at low concentrations within the sample (e.g. propane) to be made at ppm levels and below.

The HC-MOF 6 may be coiled allowing the whole apparatus to be mounted within a single boxed unit, which is compact in size. The unit may be hand-held. The apparatus may be used as a "Raman sniffer unit" to identify unwanted components in a gas sample. The apparatus may be used as a point type gas detector or sensor.

Alternatively, the HC-MOF 6 may be uncoiled and external to the main instrument housing. The apparatus can then be used as a distributed sensor with the distal end of the fibre 6 acting as the main gas collection point.

CLAIMS

1. Apparatus for analysing gas samples comprising:

a monochromatic or near monochromatic light source;

a hollow core micro-structured optical fibre, HC-MOF, in optical communication with the light source, the HC-MOF containing a gas sample to be analysed;

a diffraction grating to disperse a Raman signal from the gas sample;

a detector in optical communication with the fibre for detecting the Raman signal, the detector comprising an array of pixels arranged so that each pixel detects a specific frequency of the Raman signal,

wherein a mask is mounted between the grating and the detector to attenuate the light reaching one or more selected pixels of the detector.

2. The apparatus of claim 1 wherein the one or more selected pixels correspond to one or more peaks in a Raman spectrum of one or more components of the gas sample that are present in high concentration.

3. The apparatus of any preceding claim, wherein the attenuating mask reduces but does not eliminate the light reaching the one or more selected pixels of the detector.

4. The apparatus of any preceding claim, wherein the mask is constructed from a dynamically adjustable material.

5. The apparatus of any preceding claim, wherein the pixels of the detector are selected for attenuation by simulation of the system to identify the expected peaks in the Raman signal.

6. The apparatus of any preceding claim wherein the gas is natural gas and the selected frequencies correspond to the Raman spectrum of methane.

7. The apparatus of any preceding claim, wherein the HC-MOF has a tubular design.

8. The apparatus of any preceding claim, wherein the HC-MOF has one or more laterally located apertures to allow the gas sample to flow into or out of the core.

9. The apparatus according to any preceding claim, wherein the gas inside the HC-MOF has a differential pressure along the HC-MOF to generate a longitudinal gas flow in the HC-MOF core.

10. The apparatus of any preceding claim, wherein the HC-MOF is uncoiled.

11. The apparatus of any preceding claim, wherein the light source, HC-MOF, mask and detector are mounted in a portable unit.

12. The apparatus of any preceding claim, comprising a plurality of HC-MOFs for monitoring gas from multiple sources.

13. The apparatus in the proceeding claim comprising a plurality of HC-MOFs each connected to the same detector.

14. The apparatus of any one of claims 1 to 11, further comprising:

an alignment mechanism for coupling light from the light source into the HC-MOF, which can move a lens relative to the HC-MOF; and

a power meter placed at the distal end of the HC-MOF,

wherein alignment is achieved by moving the lens relative to the HC-MOF to maximise the signal detected by the power meter.