

Stand-off Raman spectrometer for identification of liquids in a pressurized gas pipelines

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Abstract: a stand-off Raman spectrometer has been developed to make observations of liquid samples within a gas pipeline. The instrument is based on a static Fourier Transform spectrometer. The high etendue offered by the instrument enabled four liquid samples to be measured from a distance of 2.4 m within a gas pipeline. Liquids were identified with depths less than 5 mm demonstrating that the concept is viable for active pipeline measurement.

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References and links

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1. Introduction

Liquids in gas pipelines are recognized as a major issue [1]. Natural gas processing to remove water vapour, carbon dioxide and hydrogen sulphide requires the injection of liquids into the gas stream. If these are not removed in a consistent and effective manner, they can cause significant damage to compressors and other plant in the gas transmission system. Rapid detection and identification of liquids at custody transfer points in the gas distribution network allows buyers and sellers of gas the tools necessary to take rapid operational decisions to minimize contamination of gas pipelines. Therefore, in situ measurement to identify the substance offers operators a rapid determination, and possible diagnosis, of the process problem without taking samples and waiting several hours, or sometimes days, for results. The identity of the liquid can be crucial as it may vaporize in the system or remain in liquid phase, depending on the nature of the liquid, in which case direct user intervention may be required. Currently no device is available to make this measurement, given the operational limitations. One possible instrument solution to this problem is to use Raman spectroscopy as the technique is non-invasive, and does not require a sample to be taken from the pipeline for

laboratory analysis and which has become cost effective in recent years. However, the Raman effect is very weak, and thus conventional systems cannot provide sufficient signal to noise on the time scales required, given the environmental constraints. As part of the operating criteria, any instrument used to identify the nature of an unwanted liquid must not interfere with the gas stream and must be mountable on any pipeline. The instrument must also interface with existing infrastructure. Gas pipelines are often buried, and can only be accessed from a standoff pipe, which can be up to 2 m in height, therefore any device must be capable of making observations from at least this distance. This fact does have the advantage that the optical surfaces are remote from the liquid contamination flowing in the main pipeline, which should help lower maintenance requirements. Given the weak nature of the Raman response, it is imperative that all the photons are collected from the target. This implies the spectrometer must have as high an etendue as possible if the measurements are to be successful. Also, the instrument itself must be compact and robust if it is to be mounted on pipelines around the globe. To achieve this performance a Raman instrument using a static Fourier Transform spectrometer, known as a spatially heterodyne spectrometer (SHS) [2], was developed. Figure 1 shows the basic assembly of the spectrometer. The instrument is assembled in a Michelson interferometer configuration with the mirrors replaced by reflective diffraction gratings. The two wavefronts from the grating pass through the beamsplitter, and then interfere to form a fringe pattern in space that can be Fourier Transformed (FT) to extract the spectral information.

The key advantage of this spectrometer design is that, for a given resolution it provides greater than 100 times increase in the etendue [3] than can be achieved with a traditional dispersive system and, unlike a traditional FT spectrometer, it has no moving parts. The resolving power of the instrument is essentially the number of lines illuminated at the grating surface given by:

$$R = 2G_L W \quad (1)$$

where G_L is the number of lines per mm on the grating and W is the width of image at the grating surface. The field of view of the device is given by:

$$\Omega = \frac{2\pi}{R} \quad (2)$$

The signal to noise of a given spectral line is given by:

$$SNR = \frac{S_p}{\sqrt{\sum S_p + S + B + S_D + S_R^2}} \quad (3)$$

where S_p is the light from the target source, S is the total signal light from all lines, B is the background, or contaminant, light, S_D is the dark noise, and S_R is the detector read noise. The SHS was originally developed for high resolution measurements. The device has been used to make Raman observations [4]. Due to the multiplex disadvantage the filtering requirements are critical to the instrument performance and had to provide a suppression of better than 10^7 if the instrument was to be successful. To the knowledge of the authors, this is the first time the full etendue advantage has been exploited to make stand-off Raman measurements in a non-laboratory setting.

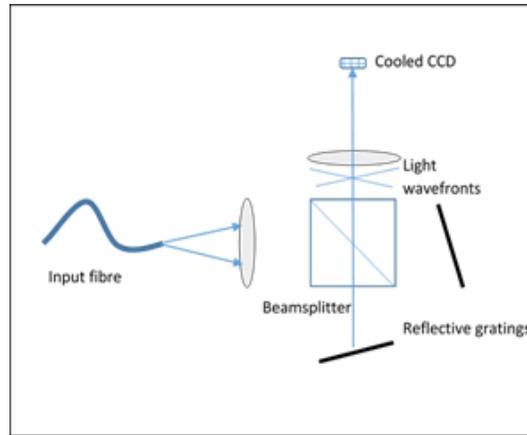


Fig. 1. Schematic of the spectrometer layout.

2. Measurement requirements

Within a gas pipeline even small amounts of liquid can generate problems, therefore any instrument must identify potentially small amounts of liquid sample (with depths less than 5 mm) in a relatively short time span (\leq less than or equal to 10 minutes), also the SNR must be greater than 5 for a clear positive detection. These pipelines are typically pressurized up to 90 Bar. The instrument is interfaced to the pipeline via bespoke designed pressurized sapphire windows. For testing, a pressurized standoff pipe was constructed. This was mounted at the GL DNV testing sites at Loughborough and Spadeadam in the UK. Due to the high pressure in the pipeline, and industry standards the maximum window diameter that could be used was 70 mm (with a 68 mm working diameter). To minimize fluorescence issues while maintaining sufficient signal levels, the operational wavelength was selected as being 785 nm. A summary of the main instrument requirements are presented within Table 1.

Table 1. Instrument requirements

Parameter	Value
Integration time	<10 min
Distance to target	2.3 m
Maximum aperture	70 mm (diameter)
Minimum amount of liquid	2 mm in depth
Resolution	4cm ⁻¹
Spectral range	400 – 2800 cm ⁻¹

The instrument was tested against five different liquids: xylene, methanol, triethylene glycol (TEG), monoethylene glycol (MEG), and a sample of compressor oil. The number of Raman photons expected from the sample is given by Eq. (4):

$$S_p = \frac{E\alpha A_T \rho d Q E t O_E}{4\pi R^2} \quad (4)$$

where E is the total number of emitted photons fired at the sample in one second, α is the molecular scattering cross section per steradian, A_T is the receiver aperture, ρ is the density of the liquid, d is the depth of the liquid, QE is the quantum efficiency of the detector, t is the integration time, O_E is the instrument optical efficiency and R is the distance to the target. ρ is assumed to be 1×10^{22} mol/cm² and $\alpha = 8 \times 10^{-32}$ cm²/sr. Equation (3) and Eq. (4) were used to define the size of the instrument.

3. Instrument design

The harsh environmental conditions expected at a number of pipelines put challenges on the Raman instrument, particularly the laser. Therefore, the instrument was separated into a projection optics suite mounted on the standoff pipe, and an instrument unit that was coupled to the instrument via a pair of 100 m length multimode fibre optic cables (Fig. 2). The operational standoff distance was approximately 2.4 m and the requirement to measure 2 mm of liquid posed significant challenges for the instrument given the weak nature of the Raman response. The collecting aperture used was a 70 mm diameter, 200 mm focal length lens that was coupled directly to a ‘receive fibre’ with a core diameter of 0.9 mm and 0.22 NA. From Eq. (4), given the restriction in the size of the entrance aperture and the instrumental requirements, a 500 mW output power laser was required operating at 785 nm. A laser line filter with a 4 nm bandwidth supplied by Semrock was used to ensure that no contaminant light was projected into the system. The laser light was coupled into the instrument via a 0.44 mm core diameter ‘transmit fibre’ with a 0.22 NA. The divergence of the projected light was 2 mrad, resulting in a 0.8 mm spot being observed at the ‘receive fibre’.

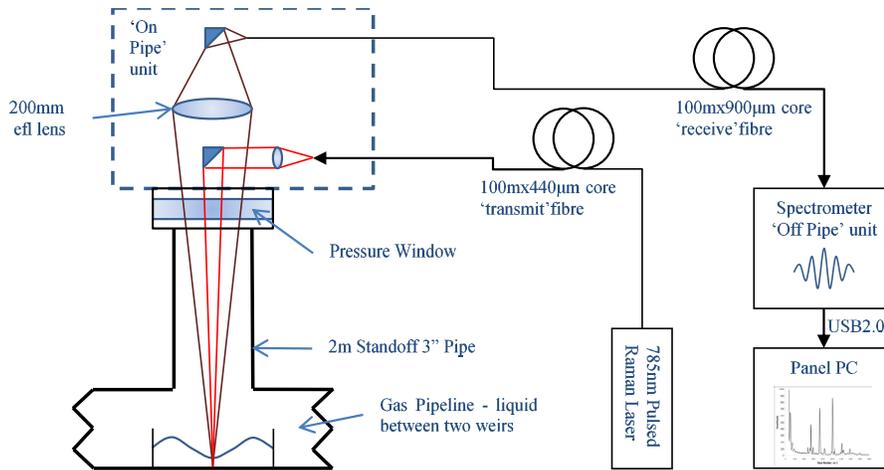


Fig. 2. Schematic of the instrument setup.

If a conventional Czerny Turner design was used, the required slit width for the resolution is given by:

$$W_s = \frac{\delta\lambda n W_p}{R_{SF} \Delta\lambda} \quad (5)$$

where $\delta\lambda$ is the target resolution in wavelength, W_p is the pixel width, n is the number of detector pixels, R_{SF} is the resolution factor (assumed to be 1) and $\Delta\lambda$ is the spectral range of the spectrometer. Therefore, to achieve the required resolution of 4 cm^{-1} , assuming the same cooled CCD was used, requires the instrument to have a slit of less than $50 \text{ }\mu\text{m}$. Therefore, using a fibre coupled Czerny instrument would have required the fibre to have a $50 \text{ }\mu\text{m}$ diameter if no light was to be lost, which would have resulted in the instrument collecting a factor of approximately 150 times less light than the SHS solution. The traditional solution to this problem is to use a fibre bundle, and stack smaller core fibres vertically at the slit. Given that the spectrometer was coupled via 100 m of optical fibre, and that no loss of light could be tolerated, using a fibre bundle was prohibitively expensive.

The large etendue advantage offered by a SHS enables a spectrometer based on this design to be directly coupled to a 0.9 mm fibre with no loss of light while achieving the required resolution. The design of the selected spectrometer used two 150 l/mm gratings, this

was imaged onto a Princeton cooled CCD with 1320×100 pixel detector and a pitch of $20 \mu\text{m}$. The CCD noise characteristics are read noise less than 5 e/pixel and a dark noise of less than $0.001 \text{ e/pixel/sec}$. The instrument resolution was better than 4 cm^{-1} with a spectral range of approximately 3000 cm^{-1} . A long pass edge filter supplied by Semrock was inserted into the spectrometer with an edge wavelength of 805 nm , a transmission of greater than 93% from 812 to 1200 nm , and a suppression of better than 10^6 from $300 - 790 \text{ nm}$. During testing it was found that the fibres produced a strong fluorescent background signal as observed by other authors [5], therefore a second identical long pass filters was mounted before the entrance to the ‘receive fibre’ to supplement the one within the spectrometer providing a net suppression of better than 10^{11} . The instrument specifications are presented within Table 2.

Table 2. Instrument Design Specifications

Parameter	Value	Notes
Source	Luxx Master Raman laser	
Operating wavelength	785 nm	
Power	500 mW	
Divergence	3-4 mrad	
Receiver	200 mm FL Fused silica doublet lens	
Diameter	68 mm	
Window	Sapphire window	80 mm outside diameter
Fibre aperture	0.9 mm	Receive fibre
Fibre NA	0.22	
Spectrometer	HES 2000	
Diffraction grating	$2 \times 150 \text{ g/mm}$ $25 \times 25 \text{ mm square}$ Princeton PIXIS 100	10 mm aperture used
Detector	$1340 \times 100 \text{ pixels}$ $20 \mu\text{m pitch}$	
Dark noise	0.03 e/pix/sec	
QE at 900 nm	50%	

An image of the final mounted system is given in Fig. 3. The spectrometer and laser were mounted within a “measurement hut” located approximately 40 m from the pipeline. The Raman spectrometer was integrated with a larger sensor suite including a liquid depth sensor before being mounted on the pipeline [6].

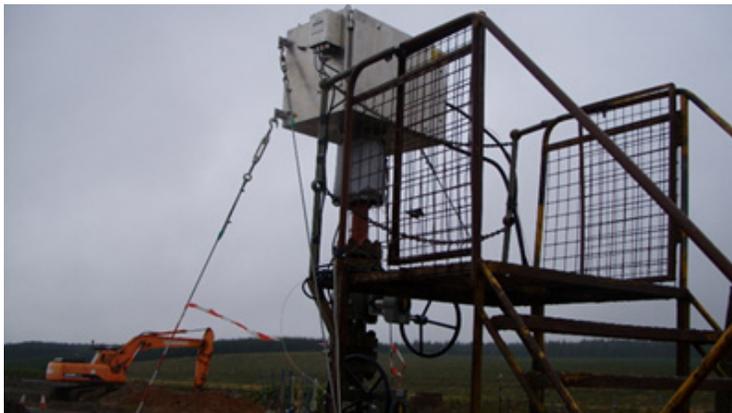


Fig. 3. The instrument measurement unit, mounted on the pipeline at Spadeadam.

4. Experimental results

The instrument was tested against all five target liquid samples; each sample was introduced to the pipeline via a pump mounted on the underside of the pipe. To minimize the amount of

liquid required two weirs were constructed inside the pipe section, as shown in Fig. 2. Measurements were made at liquid depths from 2 mm up to 20 mm. Figure 4, shows the returned power spectra acquired from each liquid in the pipe. Good SNR were returned for the data from all of the liquids tested. For the measurements of MEG, xylene, and methanol approximately 20 mm of liquid was present at the bottom of the pipe. Here, the integration time used was five minutes. For the compressor oil the signal strength was more intense so only a 1 minute integration period was used. For the TEG measurement, 5 mm of liquid was used, and the integration time increased to 10 minutes. Finally, a measurement was performed when less than 2 mm of xylene was present at the bottom of the pipe. All the results show the distinct characteristics of the target Raman sources consistent with previous measurements made in the laboratory.

As expected, the results from the compressor oil show a very strong broad band fluorescent signal being present, masking any clear Raman lines. Also, the signal strength was observed to be at least 5 times stronger than the other liquids. Methanol, being a simple molecule, displays only two peaks within the measurement range at approximately 1050 cm^{-1} and 1500 cm^{-1} . Both xylene and MEG Raman spectra are more complex with multiple peaks in the spectral region targeted.

Also as expected, the TEG power spectra was similar in nature to the MEG results. However, a clear difference can be seen, particularly at the line observed at 800 cm^{-1} . The signal to noise is also lower for this measurement due to the smaller amount of liquid present. The effect of reduced liquid amounts being present is best shown by the measurement of xylene when the level is less than 2 mm. A number of xylene Raman spectra features are still observed, however, the background continuum from the pipe can also be observed.

To estimate the observed signal to noise in the recovered power spectra for each liquid, the noise was calculated by measuring the standard deviation in the spectra beyond 1700 cm^{-1} . This value was then compared to the amplitude of the prominent Raman peaks, resulting in a measured SNR of greater than 1000 for 20 mm xylene, 380 for 20 mm of MEG, 400 for 20 mm of methanol, and approximately 90 for 5 mm of TEG. The SNR for xylene falls to less than 30 for the main peaks when the liquid sample is reduced to 2 mm although there is also a strong underlying background signal is also present. In each case, the performance is photon rather than detector noise limited. The results are in agreement with that expected from Eq. (3) and Eq. (4) once the profiles were converted to intensity spectra, and in excess of the required performance specifications. The observed SNR is clearly in excess of the performance targets discussed in section 2.

For xylene and methanol the spectra could be compared to previous measurements [7] and [8] proving the accuracy of the device.

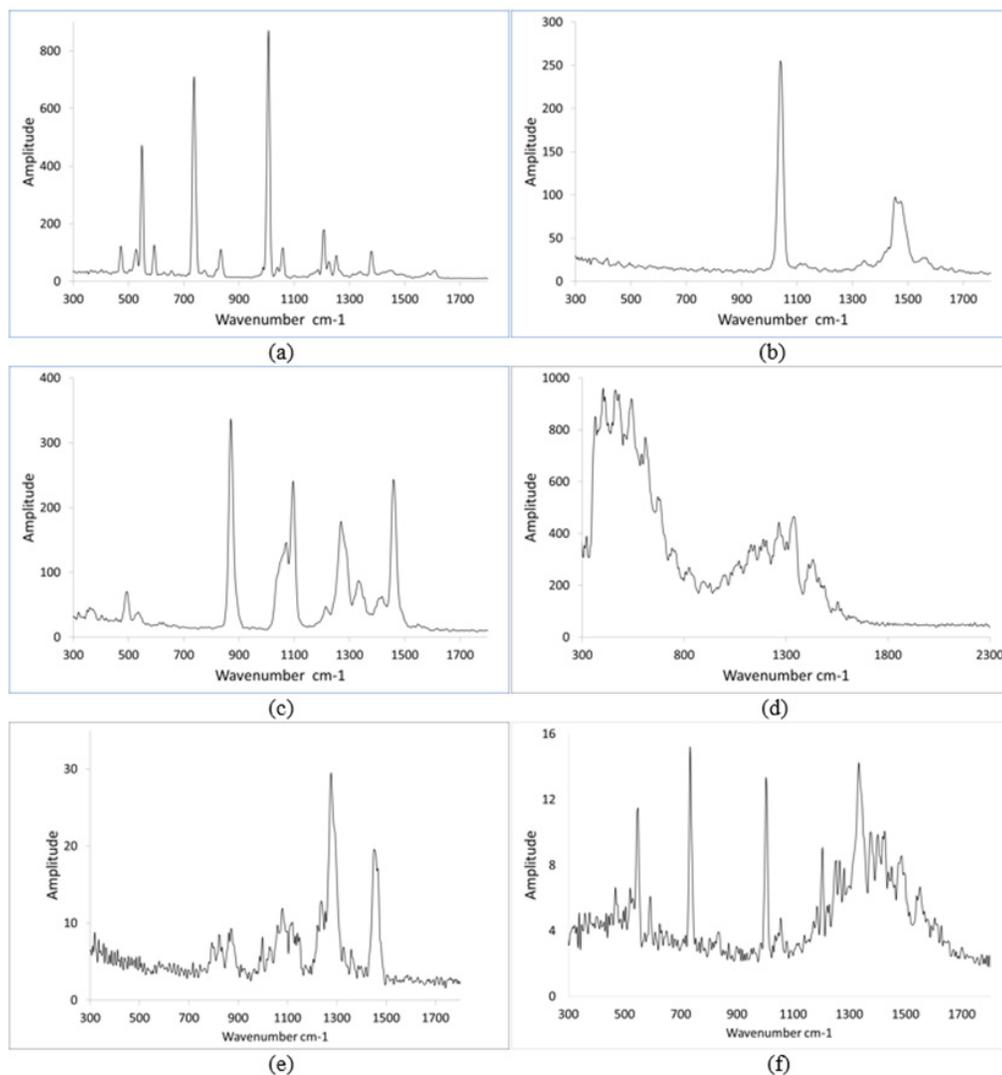


Fig. 4. Raman power spectrum measurements from liquids samples within pipeline. (a) 20 mm of xylene, integration time 5 minutes; (b) 20 mm of methanol, integration time 5 minutes; (c) 20 mm of MEG, integration time 5 minutes; (d) 20 mm of compressor oil, integration time 1 minute; (e) 5 mm of TEG, integration time 10 minutes; (f) less than 2 mm of xylene, integration time 10 minutes.

5. Conclusions

A new class of Raman instrument, based on a spatial heterodyne spectrometer, has been demonstrated. The instrument has shown the ability to identify liquid samples in a gas pipeline with samples of xylene, MEG, TEG, methanol and compressor oil being measured. The measurements have been made from a standoff distance of 2.4 m with liquid sample depths varying from 2 to 20 mm, and within the required integration time for the observations of less than 10 minutes. The superior etendue given by the instrument allows all the light to be gathered and collected within a 0.9 mm aperture fibre.

This system can offer gas processing operators rapid detection and identification of liquid contamination events, and could be used for in-line analysis of mixed phase and liquid phase pipelines to determine both trace and percentage level constituents of the liquid flows.

The system is now ready for full integration onto an active pipeline for extended trials examining factors such as usability and reliability.

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