# Experimental investigation of a new 3 mm Fibre compatible Raman spectrometer (HES 2003)

## Diary entry 15/1/15

## First demonstration

Ref: HES-ISI-RP-0010 01

Following the assembly of the spectrometer, main tests to confirm the performance of the system in a transmission Raman configuration are now able to be conducted. To reiterate from the earlier entries: The plan is to collect light from the Transmission Raman assembly via a variety of fibres of different apertures (core diameters), and measure the required integration time to achieve a pre-determined signal level at a constant resolution. In a classic spectrometer design (assuming no slit is mounted) the increase in fibre diameter results more collected light but at a cost of reduced resolution. For a target resolution of 4 $cm^{-1}$, a slit width of 100 µm of less is required when using a Czerny turner device. .

By using a transmission Raman setup, it is guaranteed that the etendue of the target light will be large. With light coming from a significant fraction of the tablet surface area and acting as a Lambertain scatterer.

The range of fibres available for the experiments is given in Table 1. The fibre lengths were 2 m, had SMA connectors, with the exception of the 3 mm bundle which was terminated with a custom ferrule mount. The 2 mm and 3 mm dimeter fibres where both constructed from a series of 550 µm core fibres.

**Table 1** List of Fibres

| Fibre Diameter | Fibre Na | Type / Notes |
|---|---|---|
| 3 mm | 0.22 | Bundle 17 fibres with 0.55 mm core diameter NA of 0.22 |
| 2 mm | 0.22 | Bundle 7 fibres with 0.55 mm core diameter NA of 0.22 |
| 1 mm | 0.39 | Multimode |
| 0.91 mm | 0.22 | Multimode |
| 0.6 mm | 0.22 | Multimode |
| 0.55 mm | 0.22 | Multimode |
| 0.4 mm | 0.39 | Multimode |
| 0.2 mm | 0.39 | Multimode |
| 0.05 mm | 0.22 | Multimode |

The measurements where made against a 3 mm thick paracetamol tablet. The tablet was illuminated with 1 mm dimeter laser spot at 785 nm. The laser power was 500 mW. The light capture assembly used two 50 mm focal length lenses with an NA of 0.22 to match the fibres.

This ensured that when the higher Na fibres were used, the higher modes where not excited. So the light that exited the fibre had an NA of approximately 0.22.

Initially the system was set up with the 2 mm fibre bundle and the spectra from a paracetamol tablet measured (Figure 1). The integration time used was 2.5 seconds giving an average counts per pixels of 3970. This ensured high signal to noise was achieved allowing spectra acquired from other fibres could be directly compared.

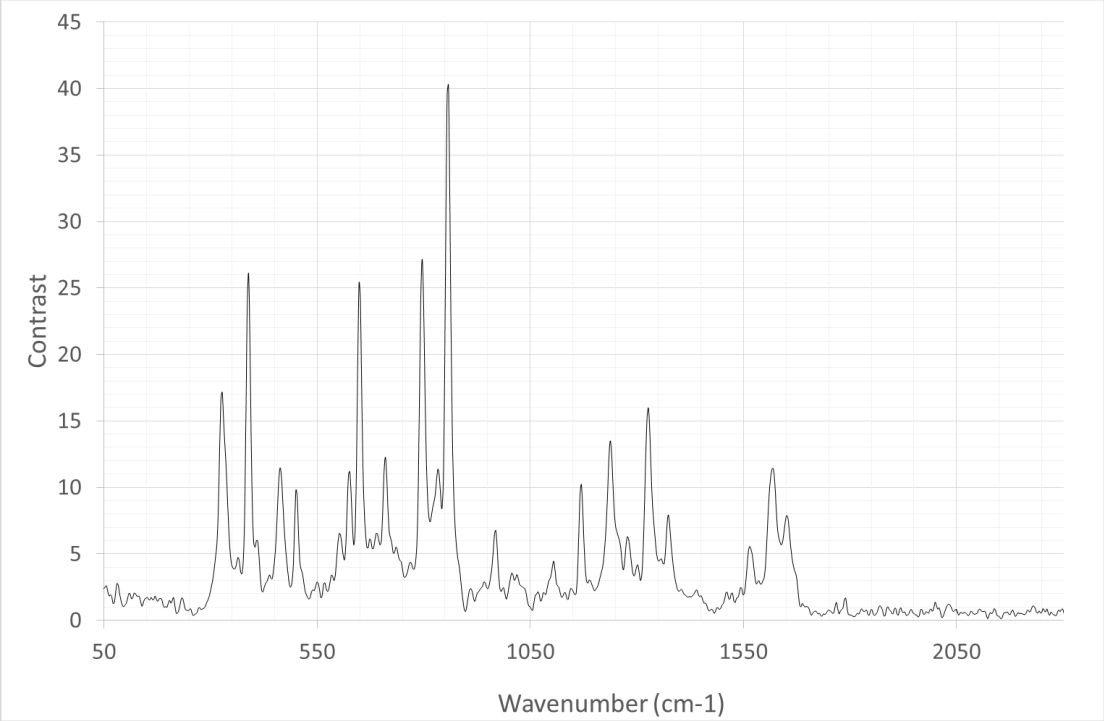


Figure 1 Paracetamol spectra, light coupled via a 2 mm fibre bundle.

The fibre was then replaced with a multimode 0.91 core dimeter fibre, the integration time was adjusted (to 5.1 seconds) in order to observe the same number of counts. The resulting spectra is given in Figure 2.

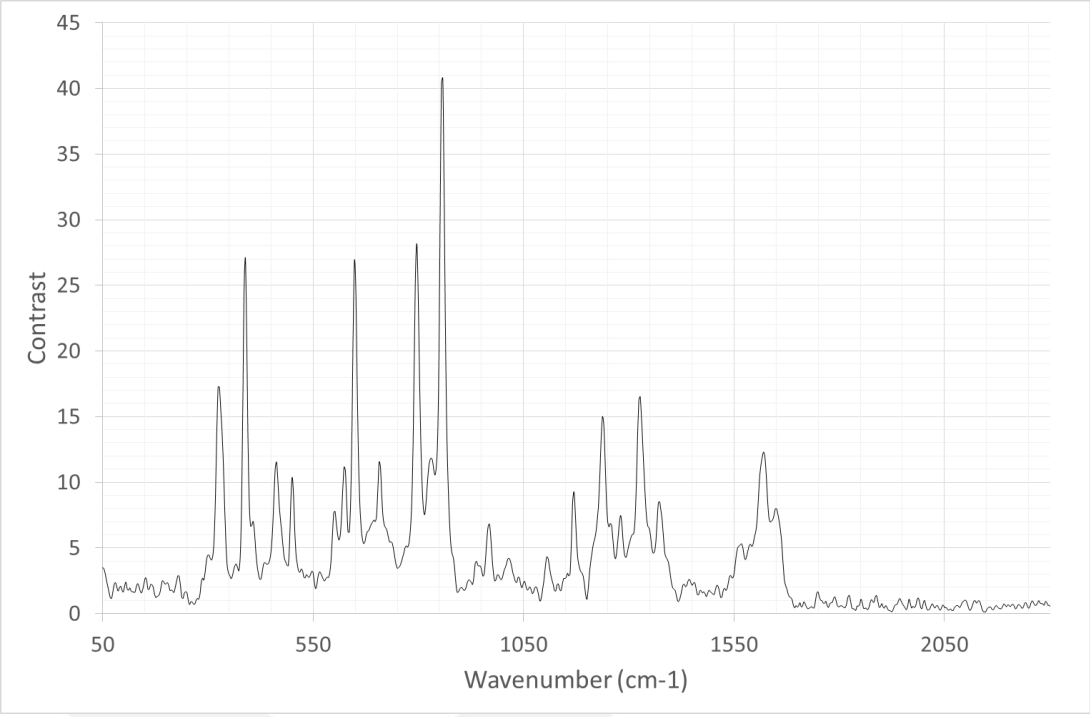

**Figure 2** Paracetamol spectra, light coupled via a 0.91 mm core fibre

This process was repeated for all of the fibres. When using the 3 mm fibre bundle the coupling assembly had to be adjusted to allow the 3 mm ferrule to be used. The resulting spectra is given Figure 3. The required integration time in this instance was 1.09 seconds.

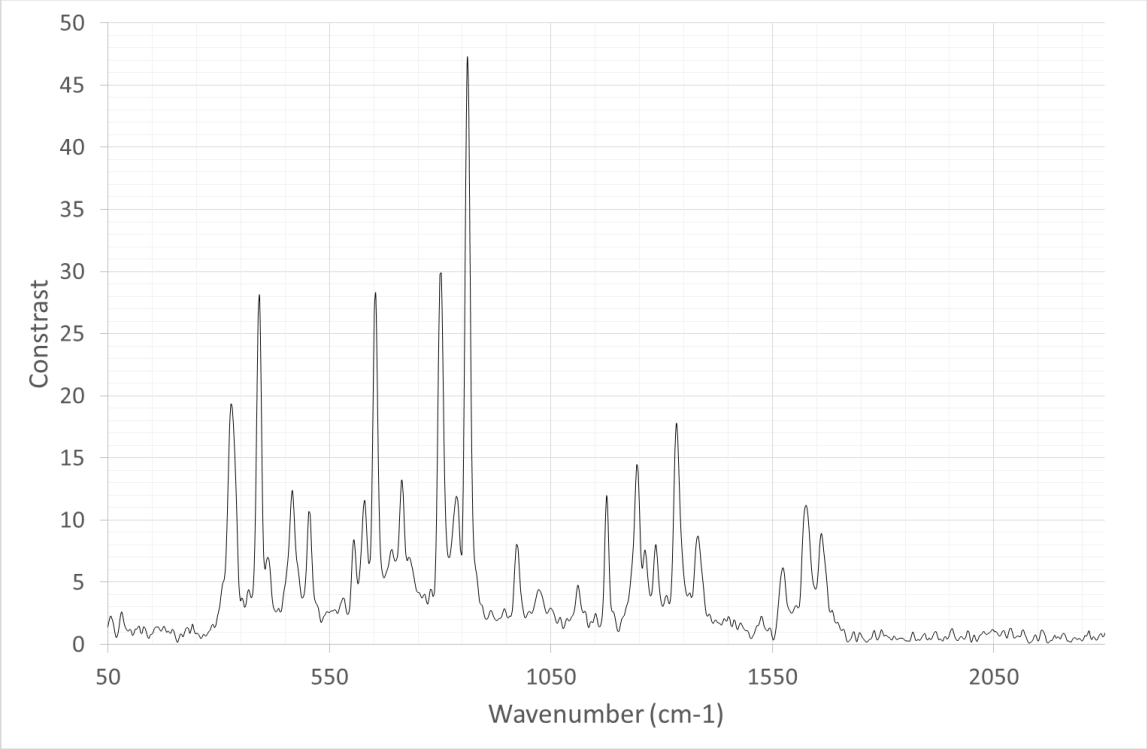


**Figure 3** Paracetamol spectra, light coupled via a 3 mm fibre bundle

Figure 4 shows the required integration time to observe 3970 counts per pixel for each of the fibre as a function of fibre diameter. The black line represents the observed results and the red line shows the calculated levels. These level were calculated form the 2 mm fibre bundle observation, it should be noted that for the two fibre bundles 47 % (2 mm bundle) and 43 % (3 mm bundle) of the light is lost due to the area not being fully filled.

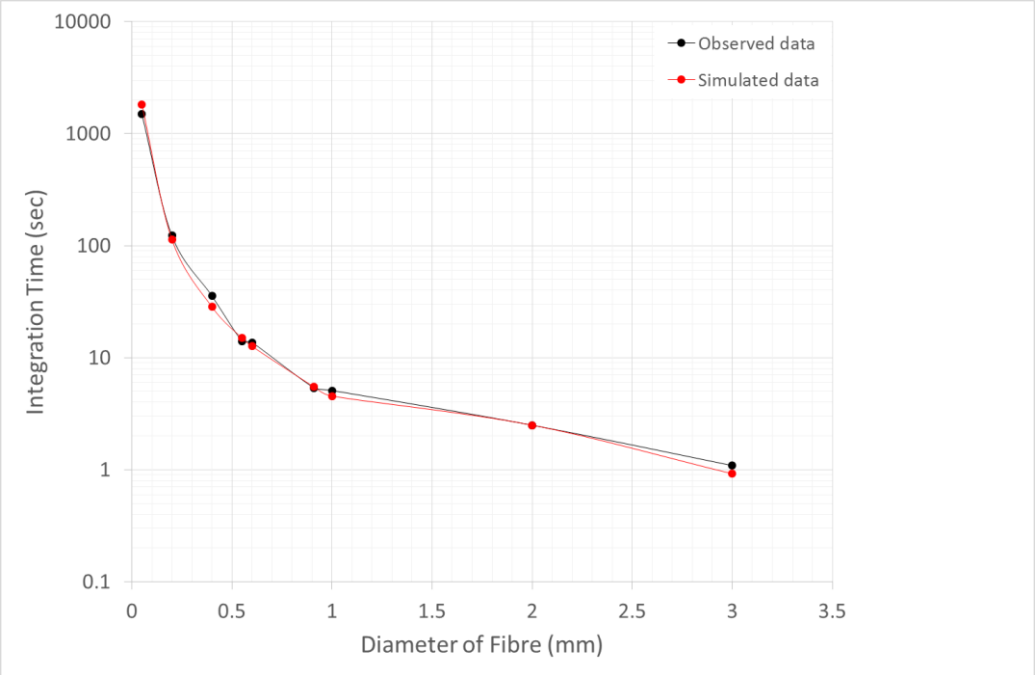


Figure 4 Required integration time to observe 3970 counts per pixel as a function of fibre diameter (Red line = simulated data; Black line = Observed data)

The observed data is a good agreement with the calculated response across the range. This is further illustrated within Figure 5. The data throughout the tests is within 1 % of that expected. However the 400 µm fibre consistently demonstrated slight poorer performance than expected. After inspection it was determined this was due to slight damage to one the fibre SMA connectors.

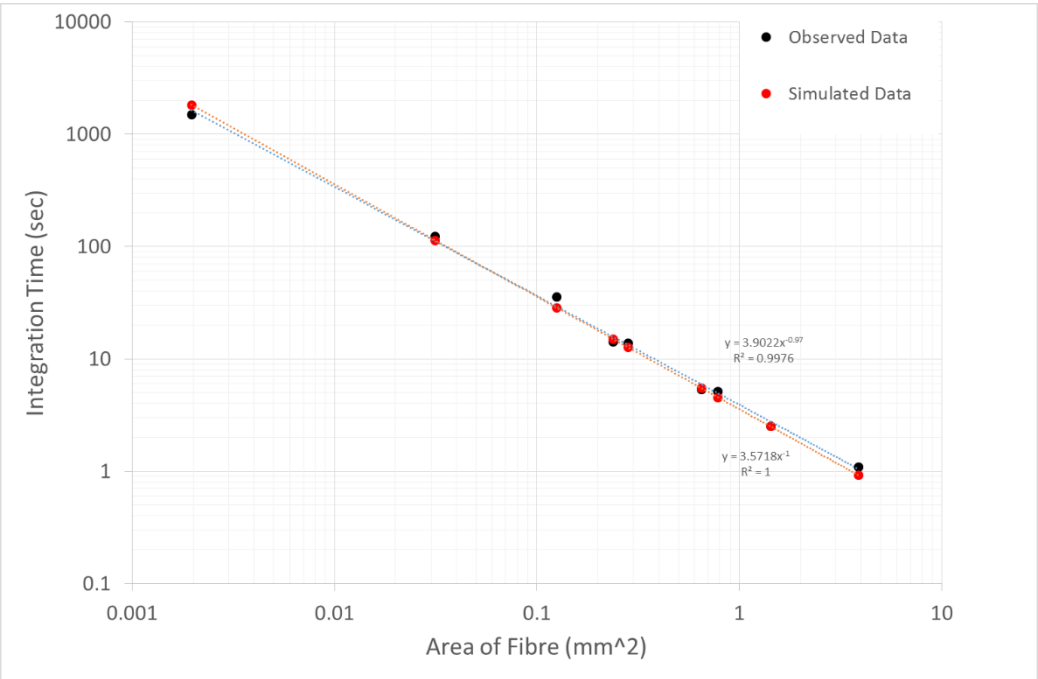


Figure 5 Required integration time to observe 3970 counts per pixel as a function of fibre area (Red line = simulated data; Black line = Observed data)

**Part two of experiments stand-off Raman**

Given the success of these experiments a stand-off configuration was also used, as illustrated in Figure 6. The tablet was located approximately 70 mm from the mono-axial LIDAR arrangement. The laser spot at the tablet was~ 1 mm in dimeter, and the telescope focused at the surface of the tablet.

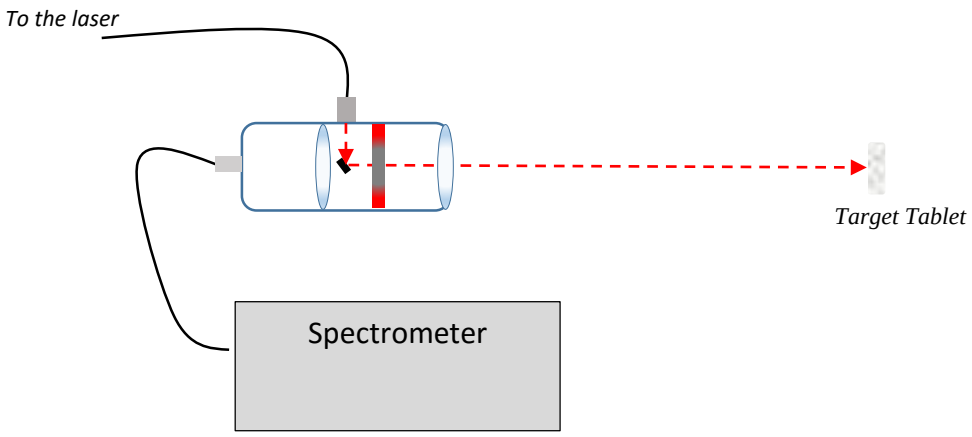


Figure 6 Stand-off Raman setup

As expected, the signal levels were observed to be higher than when operating in a transmission arrangement. Therefore a target of 20000 counts per pixel was set. The resulting integration required for the range of fibres is shown in Figure 7.

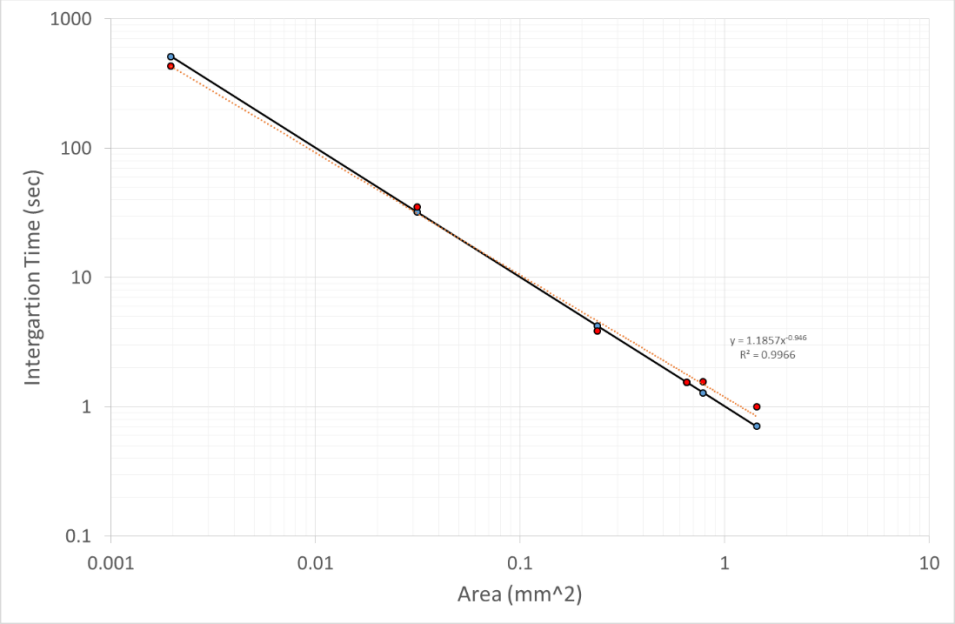

Figure 7 Required integration time to observe 20000 counts per pixel as a function of fibre area when in a stand-off configuration (Red dots = observed data; Blue dots = simulated data)

As expected there is general good agreement between the experimental and theoretical results. However, the correlation is not as strong as that observed when operating in the transmission setup. Once the fibre diameter exceed 1 mm in size the gains observed are slightly lower than that expected from the area of the fibre. This is due to the nature of the scattering surface, and the profile of the light that strike the tablet (which has a Gaussian intensity profile). When operating in transmission light is gathered from the whole tablet which emits the light with an area and solid angle product in excess of that of the spectrometer. This limits the performance of the spectrometer. In this stand-off configuration the light is Lambertain scattered from a diameter of ~ 1.5 mm. So etendue of the target is comparable or slightly smaller than the spectrometer. This shows that in this type of measurement a standard HES spectrometer with a 1 mm fibre input would be acceptable for the target observation.

The large signal returns allows us to also examine the performance of a Czerny Turner spectrometer which uses an uncooled CCD when operating in this arrangement. The spectrometer has a slit of 0.2 mm × 1 mm. Figure 8 show the resulting spectrum with an integration time of 1.55 seconds when the light is coupled to the system using the 0.91mm fibre.

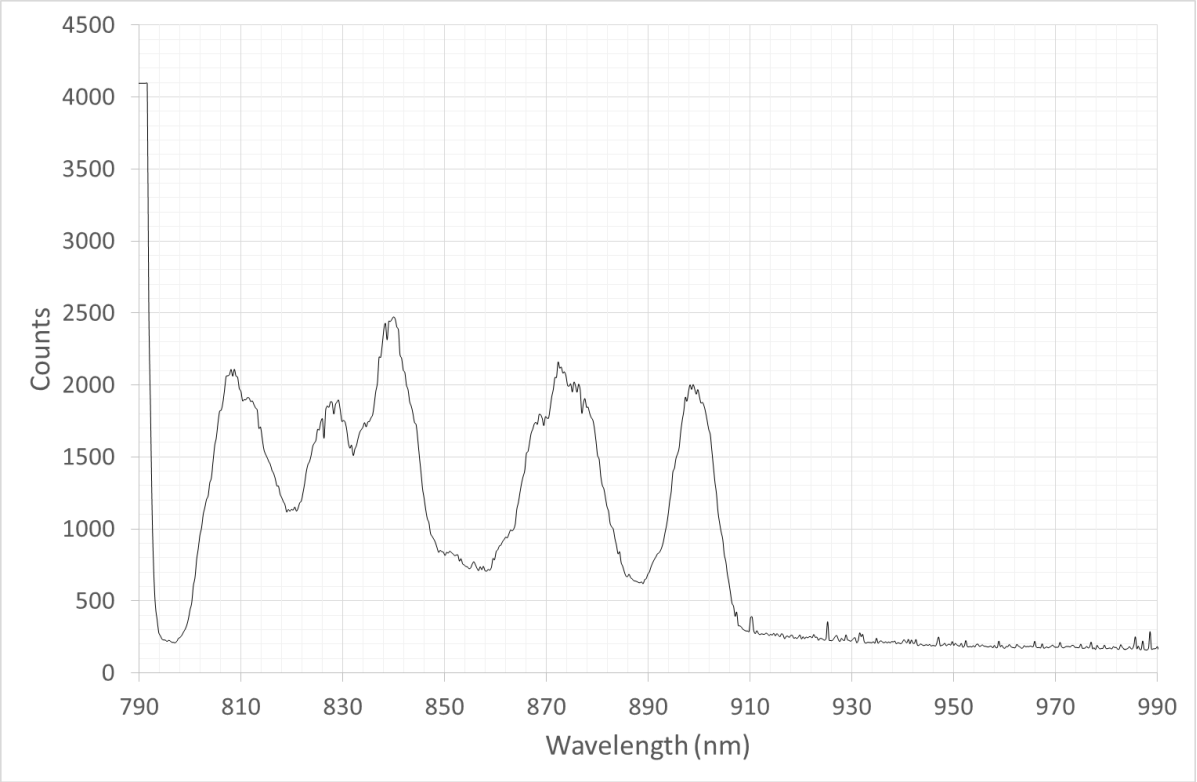


**Figure 8** Czerny turner return with 0.91 mm fibre, when operating in a stand off configuration.

Figure 8 shows that whilst the general shape of the paracetamol spectrum may be observed, the detailed information is lost. This highlights the fact that the resolution of the Czerny-Turner spectrometers are too low to resolve the features. It should also be noted that the overall counts are lower than that observed by the HES system. To increase the resolution of the Czerny Turner instrument a 0.05 mm fibre was used. The resulting spectra is shown in Figure 9, overlaid with a corresponding HES measurement and the data from Figure 8.

Despite the resolution of the Czerny Turner being improved, the signal-to-noise is too low to resolve the feature clearly. The detector only allows for a maximum integration time of 20 seconds hence the limitation.

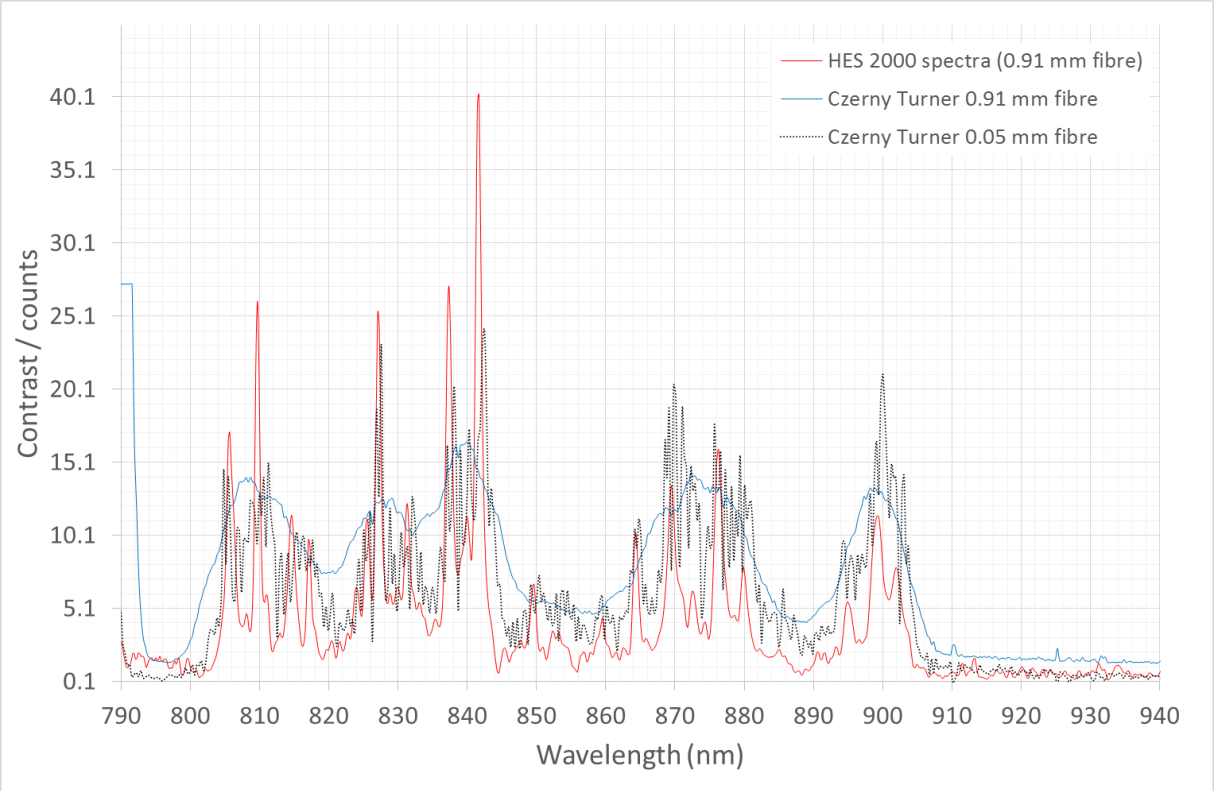


**Figure 8** Paracetamol spectra from stand-off configuration: Blue line = Czerny turner return with 0.91 mm fibre; grey line = Czerny Turner return with 0.05 mm fibre; red line = HES return with 0.91 mm fibre.

**Summary and Conclusions**

The experiment was an excellent demonstration of the systems etendue advantage, and in particular, shows how it collects more light when performing transmission Raman measurements. The stand-off results show that similar gains made when making observations in this type of setup. However, if the full advantage of the system is to be released it is important that the etendue of the target exceeds that of the instrument.

The demonstration shows that the HES range could provide key advantages in terms of speed of measurement or accuracy when making QA measurements in pharmaceutical sector. It is ideal for making bulk measurements of samples (transmission Raman), and for stand-off observations when the target sample is difficult to reach.