ChemDetect™ Analyzer Performance and Initial Alkane Measurements

Initial Observations

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Executive Summary

Two ChemDetect Analyzers (5.5 - 7.5 µm and 8.0 - 11.0 µm) were used to evaluate basic analyzer performance for baseline stability and noise, as well as wavelength stability. Spectra and concentrations for pure alkanes in nitrogen (methane, hexane, and heptane) were measured. A synthetic mixture of natural gas was also characterized. Initial results are promising for the 5.5 to 7.5 µm region, with demonstrated sensitivity and accuracy for the individual gases as well as some of the components of the synthetic gas mixture.

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Instrument Details and Setup

Two ChemDetect Analyzers, 5.5 to 7.5 µm (1336 to 1800 cm^{-1}), were deemed to be the best suited for natural gas measurements. The second tunes from 7.8 to 11.0 µm (910 to 1275 cm^{-1} and both instruments can be configured for a variety of scan ranges and step sizes. Typically full scale was used, with 0.25 cm^{-1} step size and 1.6 seconds per scan. Higher resolution tests were carried out at 0.05 cm^{-1} step size. Both analyzers have a laser linewidth of 0.5 cm^{-1}.

As shown in Fig. 1, the 5.5 to 7.5 µm region has strong, distinguishing spectra for the hydrocarbons. Moreover, it is not saturated from the high (up to 100%) concentrations of methane present in natural gas. However, this region also has strong absorptions due to water vapor, so care must be taken to ensure that the optical path is purged.
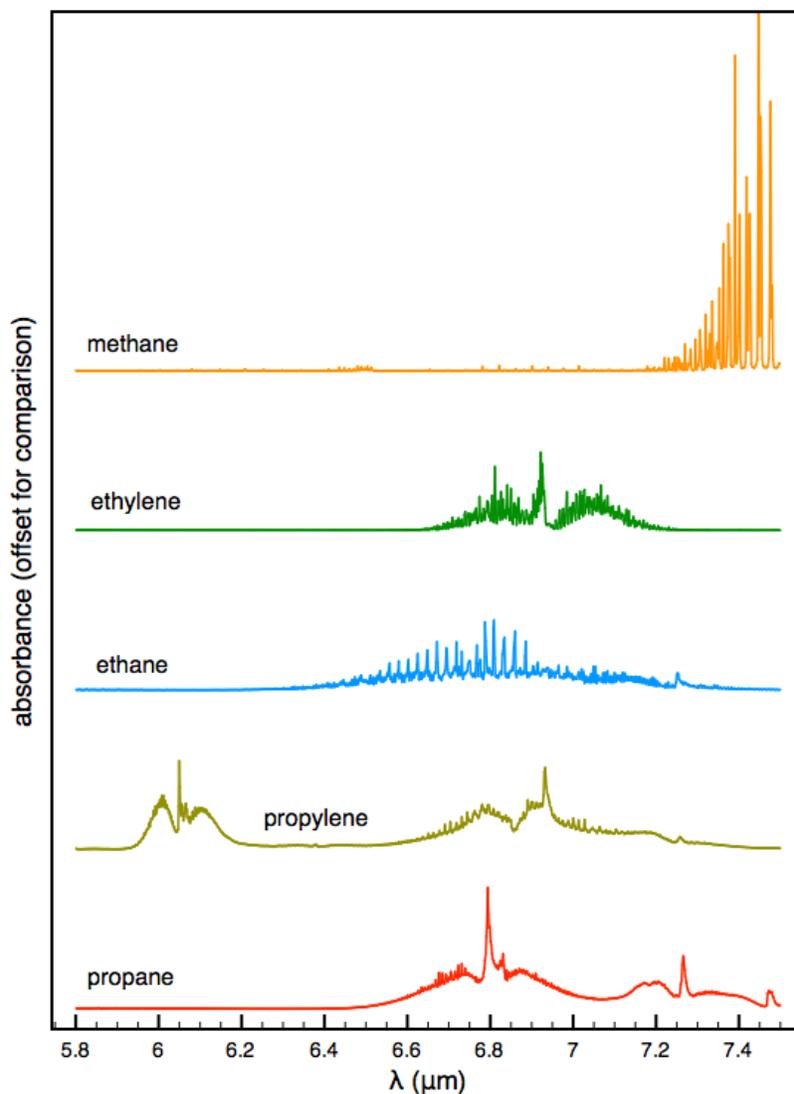
FIG. 1. Comparison of PNNL absorption spectra for the main C1 - C3 hydrocarbons in the 5.8 to 7.5 μm spectral region. Conditions: same concentration and path length for each, 25°C, 760 torr

Fig. 2 shows the path through the optical cell. The cell is a simple 15 cm single pass with CaF_2 windows. Purge (>99.9% nitrogen) or sample gas can be flowed through the cell under the control of two MKS flow meters. The analyzer was connected to a water chiller and kept at 20.0°C +/- 0.1°C for the course of the measurements.
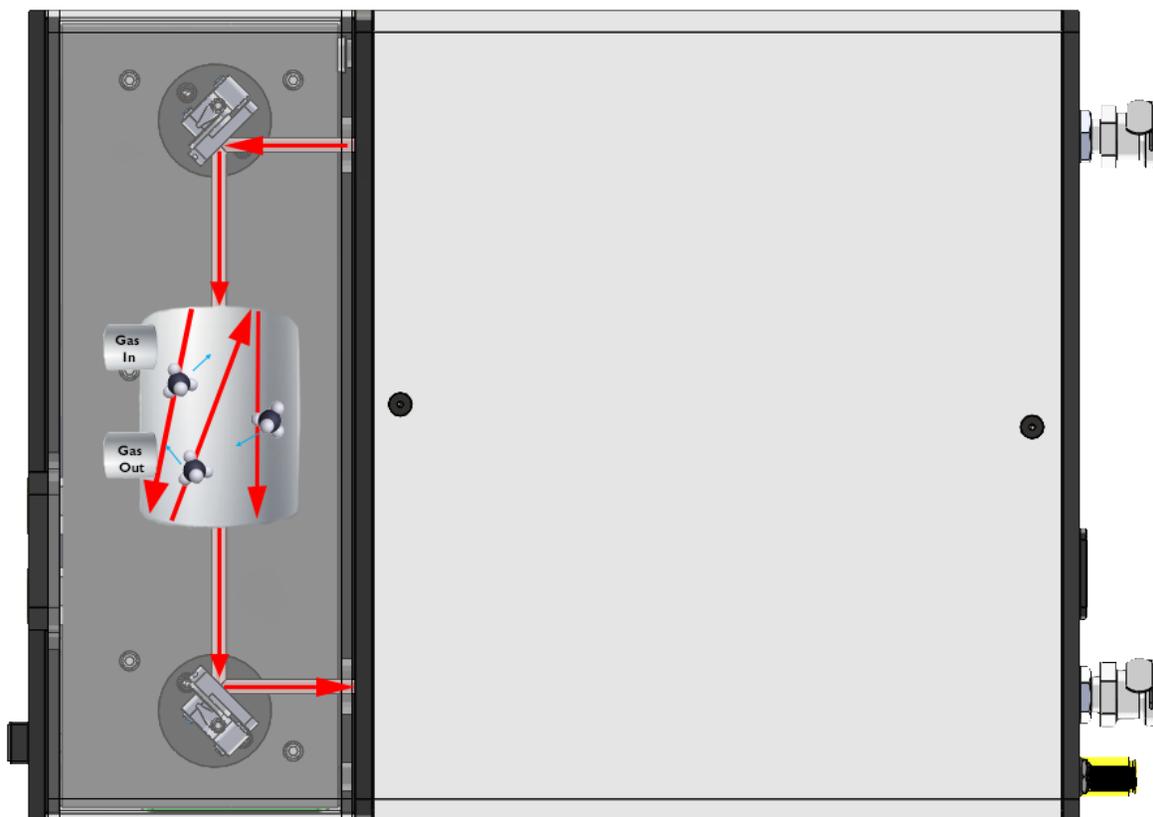
FIG. 2. Laser beam path through sample cell. The sample cell is enclosed with CaF_2 windows. Open path through atmosphere is about 30 cm. Sample gas was controlled by two flow meters, with selection between house nitrogen (>99.9%) and sample gas.

Figure 3 shows how the analyzer beam path was purged to mitigate atmospheric water absorptions. House nitrogen (>99.9%) was flowed into the purge box. It took more than an hour before adequate purge was established, then it was left in place for the duration of the measurements.
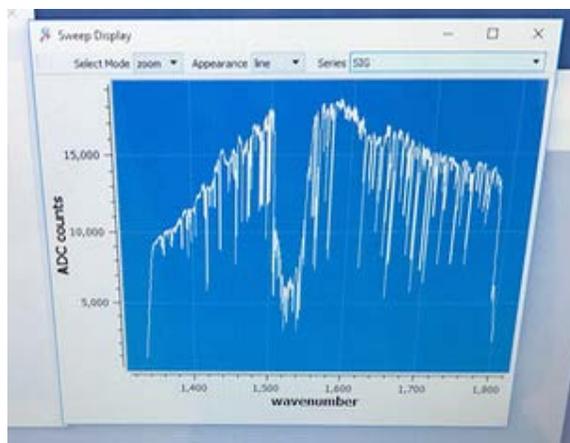
FIG. 3. Power vs wavenumber recorded on signal detector without complete purge of beam path. Note sharp down-going peaks due to atmospheric water vapor absorptions. Purge container built for analyzer. Seams of metal box sealed with Kapton tape. Gas lines, power, communication, and chiller lines routed through box seam at lower right.

The final power vs wavenumber scans (5.5 - 7.5 μm) after adequate purge had been obtained. Note the optimal power vs wavenumber on the reference detector, except at the ends of the scan, and in the 1500 - 1550 cm^{-1} region where this particular QC device has low power and a slightly less optimum power across wavenumber. This is the result of the non-optimized optical setup shown in Fig. 2. Also note the presence of small water peaks in the signal path, even after purging for 24 hours. Final instrument design will require a purged signal path similar to that achieved in the laser cavity and the reference detector, with a desiccant present to deal with residual water vapor.

Performance Tests

The first is the baseline noise and stability in the presence of a non-absorbing, or zero gas (also called 100% lines). The second is the wavenumber stability of the system over repeated scans.

Baseline noise and stability

House nitrogen (>99.9%) was flowed through the sample cell for these measurements. The ChemDetect Analyzer (5.5 - 7.5 μm) was used for all of these tests. The ChemDetect™ Software was extended to include a spectra logging feature that allows spectra to be recorded at regular intervals and appended to the data set.

Baselines were recorded for 5 minutes, with a 6 second update rate, corresponding to 4 averages. Baseline noise is 0.003 rms Naperian absorbance for a single sweep. Noise levels are higher at the scan ends, and in the 1500 to 1550 cm^{-1} range where there is lower QC power.

Wavenumber stability

Additional tests for wavenumber stability were carried out using a mixture of 6,000 ppm methane in nitrogen. A series of spectra was acquired for the full 1336 to 1800 cm^{-1} range at 0.25

cm^{-1} resolution over five minutes, while showing some of the same peaks at a much finer (0.05 cm^{-1}) step to capture the fine structure on the peaks over 30 minutes.

In both figures, the overlap is excellent, demonstrating the wavenumber stability and reproducibility.
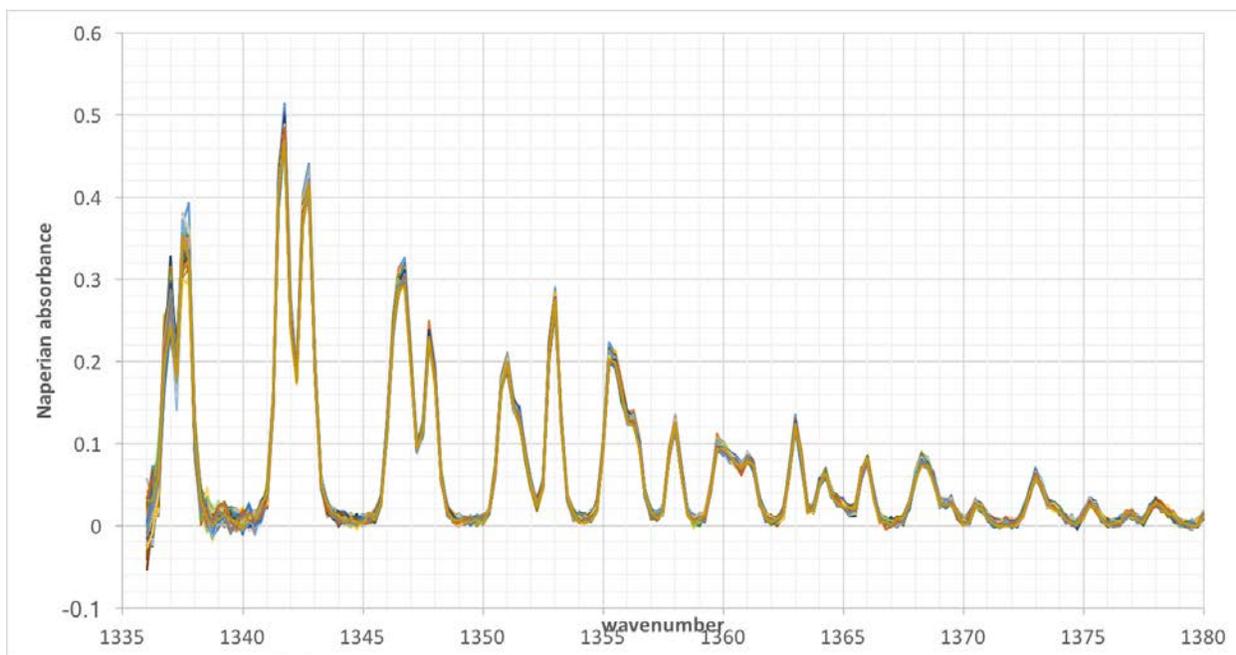
FIG. 4. Methane peaks recorded at 0.25 cm^{-1} step, 6 second interval (4 averages) over 5 minutes. Note overlap of spectral features showing stability of wavenumber axis. Gas mixture 6000 ppm methane in nitrogen. Plot shows 50 spectra overlaid.
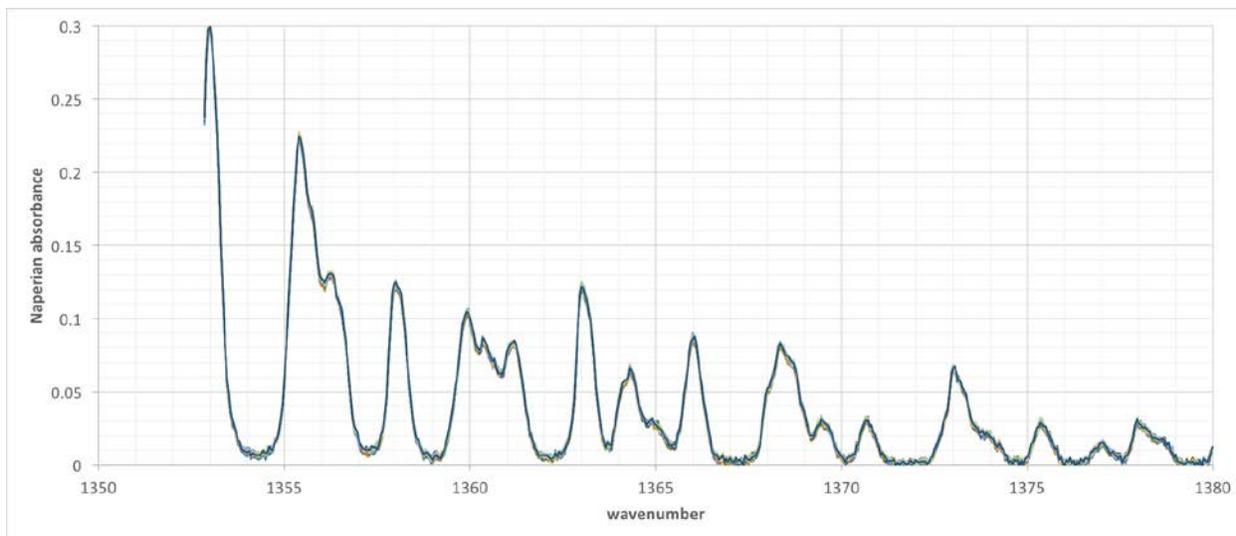
FIG. 5. Methane peaks recorded with 0.05 cm^{-1} step, 1 minute interval (37 averages) for 30 minutes. Note excellent overlap of peaks and fine structure. Gas mixture 6000 ppm methane in nitrogen. Plot shows 30 spectra overlaid.

Hydrocarbon Measurements

A series of pure hydrocarbons and a synthetic natural gas mixture were tested both for spectral fidelity and the ability to determine concentrations. The ChemDetect Analyzer is presently programmed to use a simple linear least squares fit of spectral components to determine concentration. Reference spectra from the PNNL database are taken and broadened to account for the 0.5 cm^{-1} laser linewidth, the sampled at the 0.25 cm^{-1} step of the analyzer. Since the PNNL spectra are quantitative, the absorbance values can be used in conjunction with the path length to estimate concentrations. Concentrations determined this way are acquired in a rolling fashion with the ChemDetect Software. Regions of interest are then defined to determine average concentration and rms deviation, which is taken to be the sensitivity.

Methane

A methane gas mixture of 6000 ppm in nitrogen was tested first. Samples of the resulting spectra are shown in Figs. 4 and 5. The match between measured and PNNL reference spectra is exact for peak positions, but there are some differences observed in the relative peak heights. As discussed above, these differences are consistent over time for each analyzer. However, these differences result in significant difference between estimated and actual concentrations for this methane mixture. The ChemDetect Analyzer estimated 5450 +/- 56 ppm at a 1.6 second update rate, as opposed to the actual value of 6000. However, this estimated difference remains constant, indicating that it can be calibrated out for the system by acquiring an actual methane spectrum from the analyzer, then using that for the fit with the correct concentration. This was not tried during this visit, but would be straightforward change to implement in the ChemDetect Analyzer.

Hexane
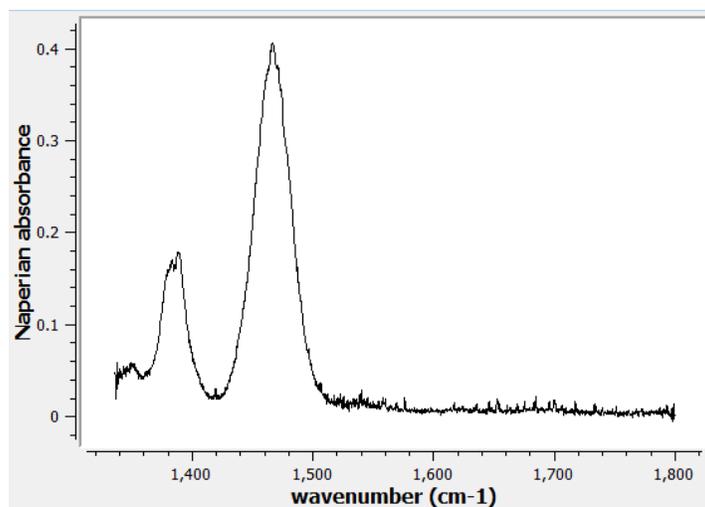
FIG. 6. Spectrum of 10,000 ppm hexane in nitrogen, 16 averages. Note residual water peaks at 0.01 absorbance level due to water in transfer line.

A gas mixture of 10,000 ppm hexane in nitrogen was tested next. The resulting spectrum is shown in Fig. 6. The match with the PNNL spectrum is excellent, and the estimated concentration from the ChemDetect Analyzer is 10066 +/- 160 ppm for a 1.6 sec update. This is very encouraging, especially since this fit was not performed against just one component; all of the alkanes were included up to hexane. Based on the uncertainties in these fit results, it is predicted that 0.01% sensitivity levels can be achieved for all of these alkanes at a relatively fast update rate. More sophisticated chemometrics and averaging should make these results consistently achievable and robust.

Interestingly, water peaks showed up along with the hexane spectrum, indicating water contamination either in the gas transfer line or the mixture itself. This raises the possibility that a natural gas analyzer in the 5.5 to 7.5 µm region could also monitor for water contamination.

Heptane
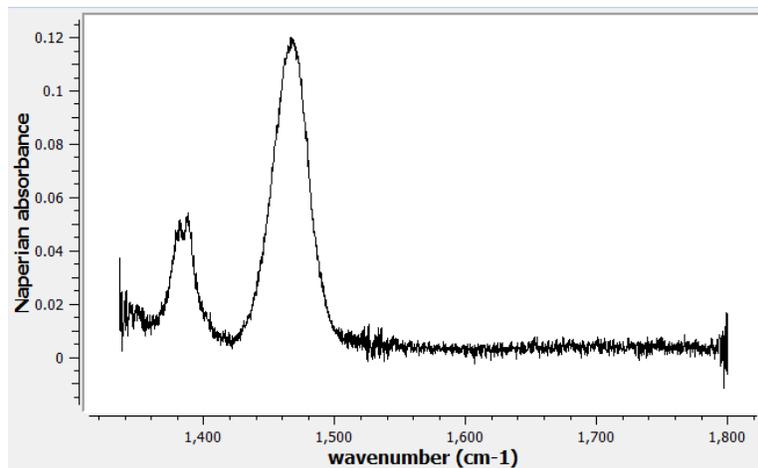
FIG. 7. Spectrum of 2,500 ppm heptane in nitrogen, 16 averages.

A mixture of 2,500 ppm heptane in nitrogen was also recorded, as shown in Fig. 7. The match with the PNNL reference spectrum is excellent. Concentration measurements were not made for the heptane sample.

Synth Gas Mixture

A synthetic natural gas mixture was obtained for the following measurements. The composition of the gas is shown in Table 1.

Table 1. Composition of synth gas and fitted concentrations.

Component	Concentration	Fit against PNNL spectra
nitrogen	2.39%	—
carbon dioxide	1.93%	—
ethane	4.80%	4.985(19)%
propane	0.963%	1.016(10)%
isobutane	0.286%	0.278(3)%
butane	0.295%	—
isopentane	0.100%	0.098(11)%
pentane	0.100%	—
hexane	0.080%	—
heptane	0.010%	—
methane	balance	49.48(41)%

The recorded spectrum for the synth gas mixture is shown in Fig. 8. As can be seen, the spectrum is rich in features. An initial attempt to fit this spectrum to obtain concentrations was performed, as described above. The fit was against standard PNNL reference spectra broadened and sampled to match the ChemDetect Analyzer linewidth and sampling step. As can be seen, the spectrum is saturated below 1380 cm^{-1}. This is chiefly due to the strong methane bands. The least-squares fit algorithm had a hard time dealing with this spectral region. That, combined with the imperfect match between the sharp features of the methane spectrum and the PNNL reference, led to the fit drastically underestimating the methane concentration, as shown in Table 1. Methane values are estimated to be half of the actual value. This matches the underestimation demonstrated for pure methane, and is certainly further exacerbated by incorrect handling of the saturated data.
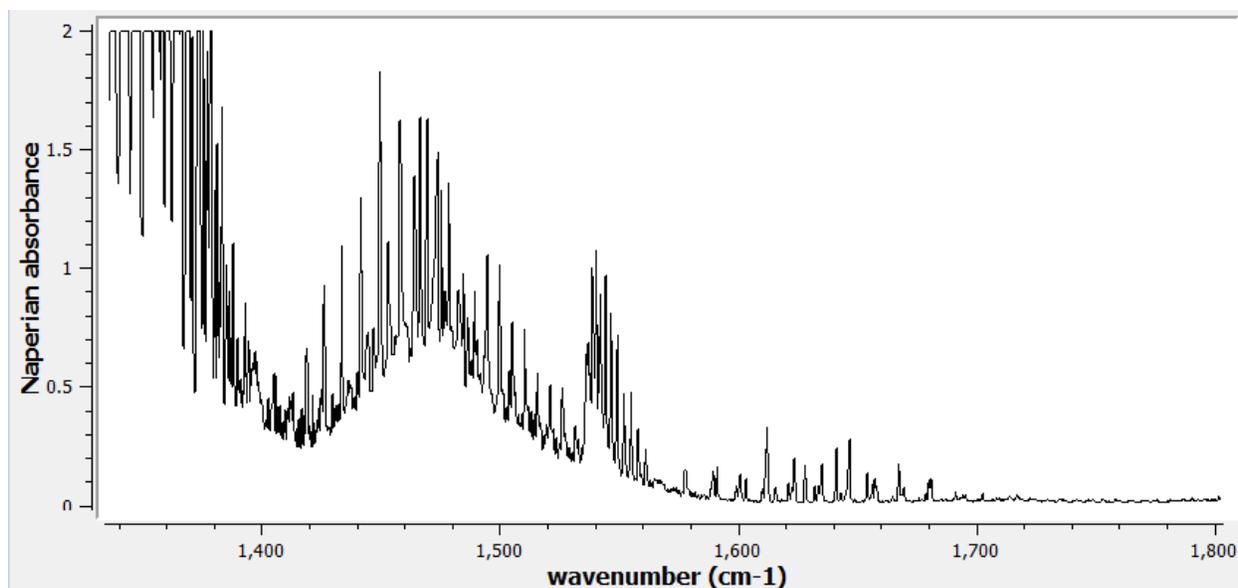
FIG. 12 Spectrum of synth gas mixture, 100 averages. Note extensive fine structure present in spectrum.

In spite of this, the fit values for ethane, propane, isobutane, and isopentane are relatively close to the actual values. The fitting algorithm can be surprisingly robust when spectral differences are significant. However, it was not possible to retrieve accurate results for normal butane and pentane, or for hexane and heptane. The mismatch of the fit and actual methane spectrum creates significant residuals that the algorithm tried to compensate for using the spectra for these species. Given the strong performance for hexane alone, it is anticipated that using an actual recorded spectrum of methane from the analyzer, and correctly handling the saturated region of the spectrum, should improve these results, and possibly yield accurate results for normal butane and pentane plus the heavier hydrocarbons, even with the simple chemometrics of a linear least squares fit.

Conclusions, Follow up

Initial results of natural gas monitoring using the ChemDetect Analyzer are promising. The 5.5 to 7.5 μm spectral region appears to be ideal, and even holds the promise of allowing moisture contamination monitoring.

The task of determining the heavier alkane fraction (hexane and higher) should be possible with better reference spectra for the light species (methane in particular) and more sophisticated chemometrics. These changes should be straightforward to implement.

Initial system performance data for baseline and wavenumber stability have been acquired. Follow-on work will include lengthier baseline scans with the analyzer using a more robust optical coupling scheme to the signal detector. This should remove the drift observed in these measurements, and allow the full FFT analysis to estimate spectral sensitivities.

Finally, the measurement setup was effective, but also highlights the need for a more controlled sample cell and optical path to realize better coupling with the signal detector, and to make the system immune to effects from external thermal variations and changes in atmospheric humidity.