

## Use of MAX-iR FTIR Gas Analyzer for Detection of Hydrocarbons in Purified Oxygen

As with any large gas manufacturer, within their arsenal of resources is a vast chain of Air Separation Units (ASUs) scattered worldwide. These ASUs act as sources for purified bulk gases such as nitrogen, oxygen, and argon. To ensure the optimal performance of these ASUs in delivering quality product, they must be continuously monitored. To give one example of concern, hydrocarbon contaminants could be present in an air separation unit due to various factors:

### Feedstock Contamination

- The air entering the ASU may contain hydrocarbons due to ambient air pollution or nearby industrial activities. These hydrocarbons can originate from sources such as vehicle emissions, industrial emissions, or natural gas leaks.

### System Leaks

- Within the ASU itself, leaks can occur in pipes, valves, fittings, or other equipment. These leaks can introduce hydrocarbons into the system, which can then be carried along with the air stream during separation.

### Contaminated Equipment

- In some cases, hydrocarbons can be present in the ASU due to the presence of hydrocarbon residues or contaminants in the equipment. This can happen if maintenance procedures are not followed diligently and improper cleaning of the equipment results.

Ideally, an ASU aims to produce high-purity nitrogen, oxygen, and other separated gases, with minimal or negligible hydrocarbon content. The presence of hydrocarbons in the process can have various implications, such as the following:

- Hydrocarbons can affect the purity and quality of the separated gases produced by the ASU. Some applications, such as electronics manufacturing or medical gas production, require extremely pure gases without any hydrocarbon contamination.
- Hydrocarbons can impact the efficiency of the ASU process. For example, certain hydrocarbons can adversely affect the performance and lifespan of process equipment, such as cryogenic systems or separation columns. Controlling hydrocarbon content helps ensure optimal process efficiency and minimize equipment degradation.

As a result, monitoring of hydrocarbons on sensitive scales (typically ppb levels) is required such that these contaminants are captured and remediated early in the ASU process. Typically, this analysis has been performed using gas chromatography/flame ionization detection (GC/FID) to detect the specific hydrocarbon impurities. However, there are drawbacks to this technology. Gas chromatographs are notoriously “fickle” instrumentation which need constant human intervention for calibration and maintenance. This is not always optimal since many ASU locations are remote and not easily serviced. In more recent years, Fourier Transform Infrared (FTIR) spectrometry has been used successfully to detect hydrocarbon impurities down to ppb levels in these streams. This has been possible due to the lack of an infrared signature in the bulk gases, hence there is no large absorption background.

The FTIRs which have been commonly used rely on a cooled Mercury-Cadmium-Telluride (MCT) detector due to their very high detection capability. The most sensitive detectors use cryogenic cooling with liquid nitrogen. However, an automated cryogenic supply system or human intervention must be used to maintain the cooling process. Neither option is reliable for remote deployment. Alternatively, thermoelectric cooling of the detector using Peltier devices is sufficient; however, these systems have a reduced infrared bandwidth, so certain regions of the spectrum cannot be probed.

Thermo Fisher Scientific has developed an FTIR spectrometer system, the Thermo Scientific™ MAX-iR™ FTIR Gas Analyzer, which does not rely on the need for detector cooling.

The MAX-iR Gas Analyzer utilizes a Deuterated Tri-Glycyl Sulfate (DTGS) pyroelectric detector which operates at room temperature, yet provides the full mid-infrared range of wavelengths for interrogation of hydrocarbons as well as other gaseous materials which could possibly be in a purified bulk gas stream.

The testing with the MAX-iR Gas Analyzer involved introducing select hydrocarbons at varying levels and combinations as shown in Figure 1. This process was used to determine if there were any interferences which could degrade detection limits and/or sensitivities in such a monitoring process.

Therefore, the detection limit and interference resistance were paramount to assessing the use of MAX-iR Gas Analyzer in this process. The primary compound used as the alarm trigger for excess hydrocarbon in the oxygen stream was propane ( $C_3H_6$ ).

## Experimental Overview

Four calibration gas mixtures in balance  $N_2$  connected to a dilution system prior to the FTIR

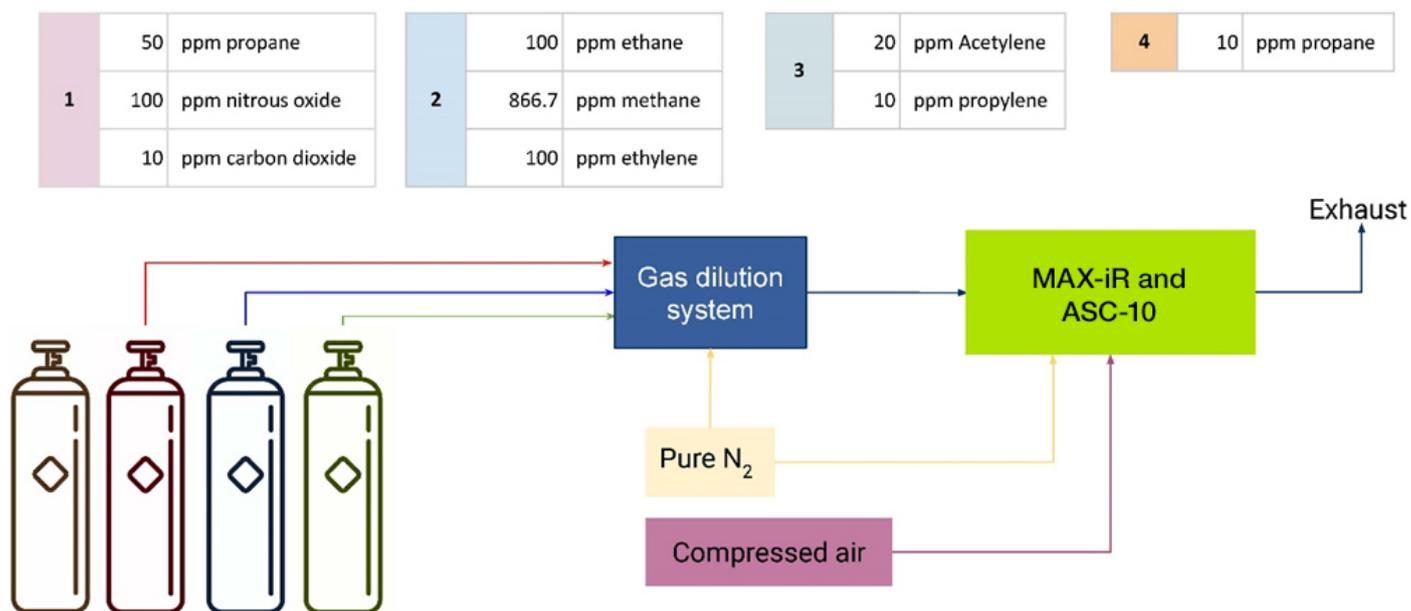


Figure 1: Experimental Overview Diagram

Three separate gas mixtures (bulk  $N_2$ ) were supplied into a gas dilution/mixing system which uses  $N_2$  as the diluting gas. In addition, two single binary gas mixes were used for calibration transfer standard (CTS) and detection limit (DL) checks.

The mixes were as follows (Table 1):

Channel 1	Channel 2	Channel 3	CTS check	DL check
50.21 ppm $C_3H_8$	100.7 ppm $C_2H_6$	20.01 ppm $C_2H_2$	899 ppm $CH_4$	10.2 ppm $C_3H_6$
99.82 ppm $N_2O$	869.4 ppm $CH_4$	0.1 ppm $C_3H_6$		
9.965 ppm $CO_2$	99.48 ppm $C_2H_4$			

Table 1: Gas Mixtures

Before running the tests, the MAX-iR Analyzer was purged overnight with N5.0 purity nitrogen in both the gas cell area as well as the optics area. The single beam was monitored to demonstrate that no residual gases were in either path. This ensures that an absolutely zero baseline with no minor artifacts will be present such that the remainder will be the residual noise of the baseline.

Multiple tests were run to determine various limits and perform validations:

1. Calibration transfer check validation against CH<sub>4</sub> (bulk N<sub>2</sub>) cylinder.
2. Calibration validation of all tested gaseous components.
3. Detection limit checks of all tested gaseous components.
4. Cross interference tests of gaseous components in separate dilution blends with varying ratios of each channel mix.
5. Component interference measurements in separate runs with randomly selected ratios of each channel mix.
6. Propane detection limit tests with dilution levels of the C<sub>3</sub>H<sub>6</sub> binary mix going from single to double digit concentrations.

## Data

To simplify the presentation of the data, we show the final results of the tests either as averages with standard deviation limits or as graphical plots to reveal any biases or deviations within interference testing. In addition, the detection limits for each of the investigated gases will be reported as well.

The first check of the MAX-iR Analyzer was a calibration transfer standard check which is normally performed on any FTIR before a series of runs. This check determines whether the FTIR is performing correctly. The observed methane concentration of 885.1 ± 0.6 ppm deviates 1.5% from the certified value of 899 ppm, which is well within the accepted variance of 5% for a normal CTS check.

The next checks were for the calibration validations using set flows of the four-channel gas mixer. Typical results for each tested gas were as shown in Table 2.

Gas	Average Deviation (%)
C <sub>2</sub> H <sub>6</sub> (ethane)	3.8±0.4%
CH <sub>4</sub> (methane)	0.9±0.4%
C <sub>2</sub> H <sub>4</sub> (ethylene)	4.0±0.3%
C <sub>2</sub> H <sub>2</sub> (acetylene)	0.4±0.1%
C <sub>3</sub> H <sub>6</sub> (propylene)	3.7±0.4%
CO <sub>2</sub> (carbon dioxide)*	4±1%
N <sub>2</sub> O (nitrous oxide)	2±1%

\*possible slight leak affecting CO<sub>2</sub> measurement

Table 2: Calibration Validation Test Results

Following the calibration validations were the limit of detection tests for all gases except for propane (Table 3). The propane test was conducted in a different manner since this gas measurement determines whether the ASU process shuts down. Therefore, a more concise determination of measurement accuracy and bias near its limit of detection was conducted in a separate experiment. During the interference testing or effectiveness (randomized interference) testing, no major interference bias of propane from most of the tested gases was noted.

Gas	Avg. LOD (3σ) ppm
C <sub>2</sub> H <sub>6</sub> (ethane)	0.11
CH <sub>4</sub> (methane)	0.05
C <sub>2</sub> H <sub>4</sub> (ethylene)	0.03
C <sub>2</sub> H <sub>2</sub> (acetylene)	0.03
C <sub>3</sub> H <sub>6</sub> (propylene)	0.08
CO <sub>2</sub> (carbon dioxide)	0.01
N <sub>2</sub> O (nitrous oxide)	0.015

Table 3: Limit of Detection Test Results

A representative sample spectrum showing all measured gas components is shown following the conclusion to demonstrate the relative overlap of the spectral response for all the components; each component is quantified correctly using least squares analysis even though their regions have many coincidences (Figure 6).

The only truly consistent measurement interference observed was a slight negative bias in the propane measurement (trending to -0.075 ppm) when exposed to high (133 ppm) concentrations of methane. This bias is shown graphically in the following plot (Figure 2).

Extended picket fencing or quantification region adjustment will likely improve this. However, being an extreme case of hydrocarbon impurity, a level like this would most likely cause ASU process alarming in any case. At reduced methane concentrations, there was little to no observed bias in propane level.

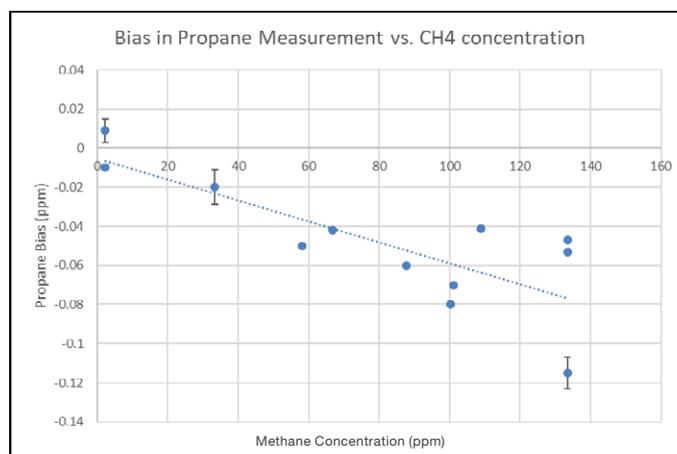


Figure 2: Bias in Propane Measurement vs. CH<sub>4</sub> Concentration

Finally, a strict propane detection limit test was performed using the binary propane/nitrogen cylinder mix. Both the response linearity and the measurement deviation from predicted are shown in the plots below (Figures 3 and 4).

A consistent 18 to 27 ppb detection limit was observed throughout this testing; this would be in alignment with the accepted detection limit of 30 ppb noted in previous testing on liquid nitrogen cooled MCT detection systems.

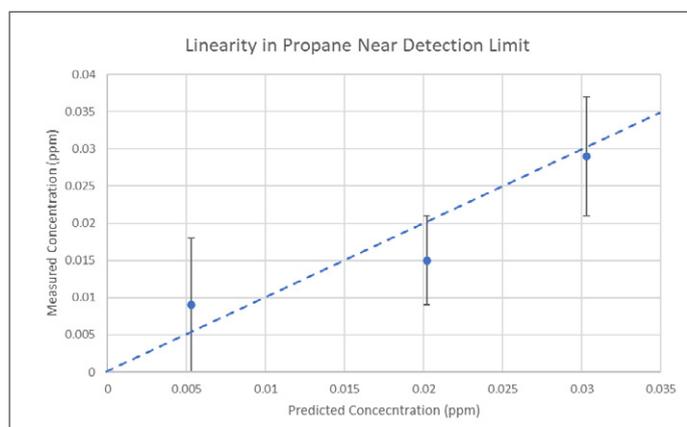


Figure 3: Linearity in Propane Deviation

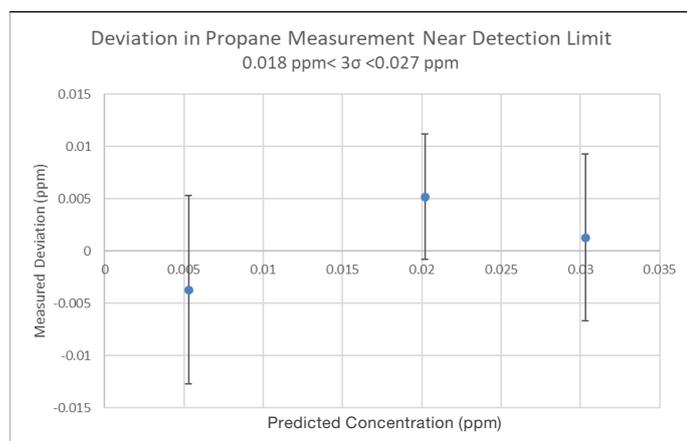


Figure 4: Deviation in Propane Measurement

## Conclusions

1. The MAX-IR FTIR Gas Analyzer performed as expected with no significant deviations in observing individual hydrocarbon concentrations in widely varying mixes.
2. There is a slight negative bias (-0.075 ppm) in the propane measurement when high methane is also present, well beyond any extreme alarm level for an ASU process. Lower levels of methane had little to no effect on the propane measurement.
3. The calculated detection limit for propane was 0.03 ppm, which is equal to that observed with a liquid nitrogen cooled MCT FTIR.
4. The performance of the room temperature DTGS FTIR system exhibits performance equal to or better than a liquid nitrogen cooled MCT based system. The lowest RMS residual noise for 1 minute integration time is on the order of 0.0001 AU (Figure 5).

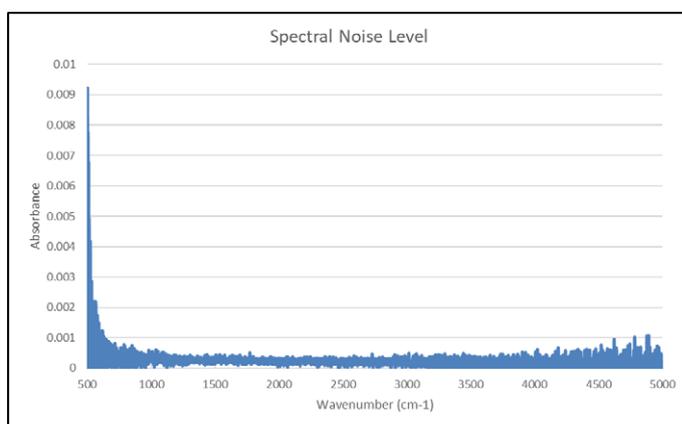


Figure 5: Spectral Noise Level

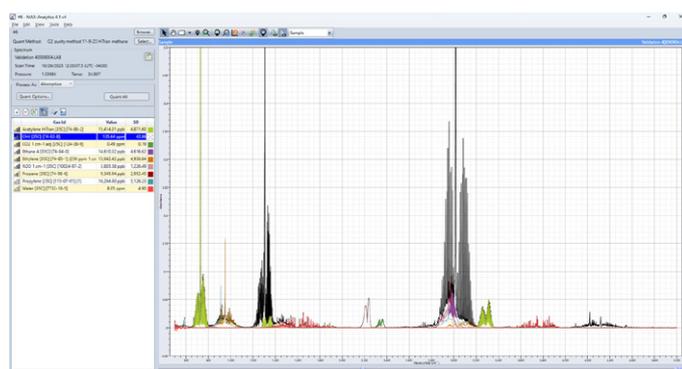


Figure 6: Representative spectrum simultaneously showing all quantified gases for this test

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