



Real-Time Simultaneous Quantitative Measurement of Methane (0-22 ppm) in Propane (0-1500 ppm) Using Encoded Photometric InfraRed (EP-IR) Spectrometry.

An EP-IR spectrometer manufactured by Aspectrics, Inc. was tested for its capacity to accurately quantify a minor concentration gas, methane (0-22 ppm) when mixed with a spectrally overlapping, majority concentration gas, propane (0-1500 ppm). PCR-based calibrations were developed, allowing for precise measurement of both components (Methane SEC = 0.2 ppm and SEP = 0.8 ppm; Propane SEC = 4 ppm and SEP = 4 ppm.)

Once calibrated, the 3-5 μm EP-IR spectrometer was used to simultaneously predict, in real-time and with a response refresh rate of 30x per second, the concentrations in methane and propane. Once the 2 gases had filled the 5-meter multi-pass gas cell at equilibrium (12 1/2 minutes @ 500 mL/min flow rate), measurement precision and repeatability was characterized by a non-weighted average bias of 3.2 ppm and 0.4 ppm and a non weighted average SDDr of 1.3 ppm and 0.7 ppm for propane (0-1500 ppm) and methane (0-22 ppm), respectively.

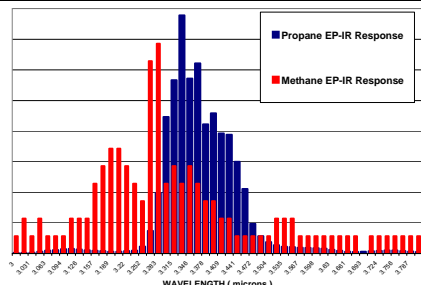


Fig. 1a: 128-channel actual EP-IR auto-scaled response for propane and methane

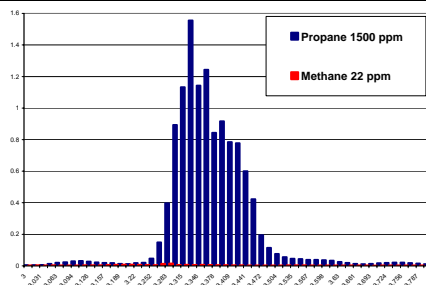


Fig. 1b: 128-channel actual EP-IR response for 1500 ppm propane and 22 ppm methane

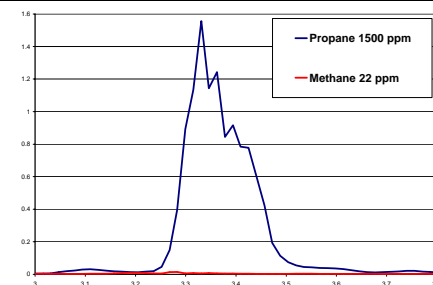


Fig. 2: "Line" representation of the 128-channel EP-IR response for 1500 ppm propane and 22 ppm methane

INTRODUCTION

EP-IR spectrometry is a new, rugged, yet analytically accurate infrared spectrometry technology specifically designed for the simultaneous measurement of multiple chemical compounds at high speed (up to 100 scans per seconds) in industrial environments.

EP-IR spectroscopy is based upon the use of an encoder disk onto which all wavelengths in a given region of interest are uniquely modulated. The final spectral intensities are computed via a Fourier transform providing access to the entire spectral information.

Current technology allows up to 256 user-defined micro-regions of the spectrum to be measured simultaneously by a single detector (multiplexing advantage), hence providing the opportunity for simultaneous quantitative analysis of several components as well as the implementation of complex, multivariate chemometrics methods.

MATERIALS & METHODS

An Aspectrics, Inc. Spectral Engine configured for the 3 – 5 μm region providing access to 128 photometric channels (each channel being 10 nm wide and with center-wavelength equally distributed every 15.7 nm in the wavelength domain) was used for this experiment. A glow-bar source and a PbSe (lead selenide) detector with single stage thermoelectric cooling were used.

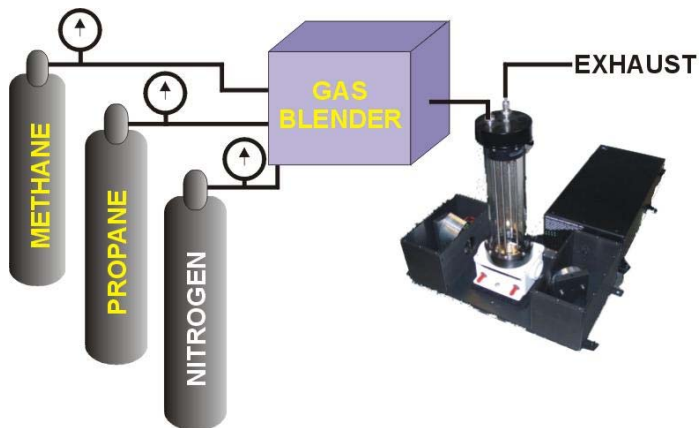
The instrument was set to collect 30 spectra per second.

The EP-IR spectrograph was mated to a method development sampling bench allowing the use of traditional FT-IR sampling accessories. In this case, a 5-meter pathlength multi-pass non-temperature controlled Specac, Inc. gas cell was used.

Gases were fed into the gas cell by means of a custom built gas blender allowing for 1% precision and set to a flow rate of 500 mL per minute. With the gas cell used, it was estimated that stable concentrations of gases in the mixture were reached after 12 1/2 minutes of flow.

Principal Component Regression calibration equations (chemometrics methods) were developed using the SID, Inc. Real-Time Spectroscopy (RTS) software application. This software application also allowed real-time application of the PCR calibration equations for the simultaneous measurement of methane and propane with a response refresh rate of 30 x per second.

Methane and propane were guaranteed pure at 99.99% and dry nitrogen (N_2) was used to purge the cell between experiments.



RESULTS

PCR Calibrations Statistics			
	R ²	Bias	SEC
Propane	1.0000	3 ppm	4 ppm
Methane	0.9997	0.2 ppm	0.2 ppm

PCR Validations Statistics			
	R ²	Bias	SEP
Propane	1.0000	3 ppm	4 ppm
Methane	0.9970	0.6 ppm	0.8 ppm

Calibrations and validations statistics showed very high levels of correlation between calculated and reference concentrations in the two gases of interest.

Moreover, SEC and SEP values were equal to or smaller than the precision of the reference method (1% precision gas blender setting). This means that the limiting factor in defining the accuracy and sensitivity of the EP-IR instrumental method was the reference method against which the instrument was calibrated.

Lastly, bias values were, in all cases, equal to or smaller than the SEC and SEP values calculated, further proving the stability of the instrumental response.

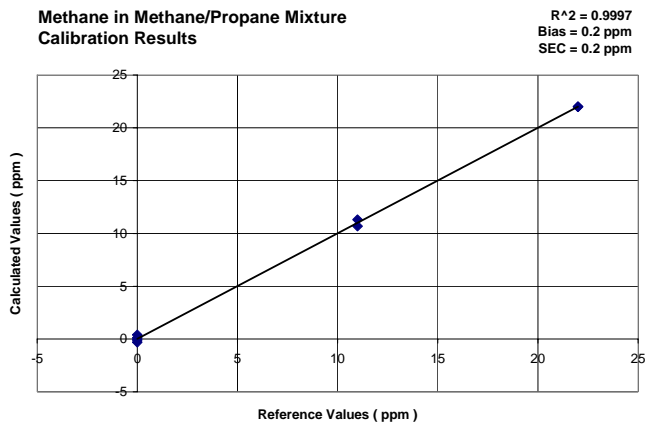


Fig. 3: Calibration for Methane (0-22 ppm) in up to 1500 ppm of propane

Three real-time validation runs were completed. Settings were:

Run #	C ₃ H ₈ (ppm)	CH ₄ (ppm)
1	1500	0
2	1500 -> 750	0 -> 11
3	750 -> 0	11 -> 22

Once the 2 gases had filled the 5-meter multi-pass gas cell at equilibrium (12 ½ minutes @ 500 mL/min flow rate), average precision of the measurement was statistically characterized by a bias of 3.2 ppm and 0.4 ppm (for propane and methane, respectively) and average repeatability of the measurement was statistically characterized by a Standard Deviation of Differences for Repeatability (SDDr) of 1.3 ppm and 0.7 ppm (for propane and methane, respectively.)

Repeatability	MDr (Bias)	SDDr
⇨ Propane 0 ppm	5.1 ppm	0.4 ppm
⇨ Propane 750 ppm	0.1 ppm	0.8 ppm
⇨ Propane 1500 ppm	4.4 ppm	2.7 ppm
⇨ Methane 0 ppm	1.2 ppm	0.8 ppm
⇨ Methane 11 ppm	0.0 ppm	0.6 ppm
⇨ Methane 22 ppm	-0.1 ppm	0.6 ppm

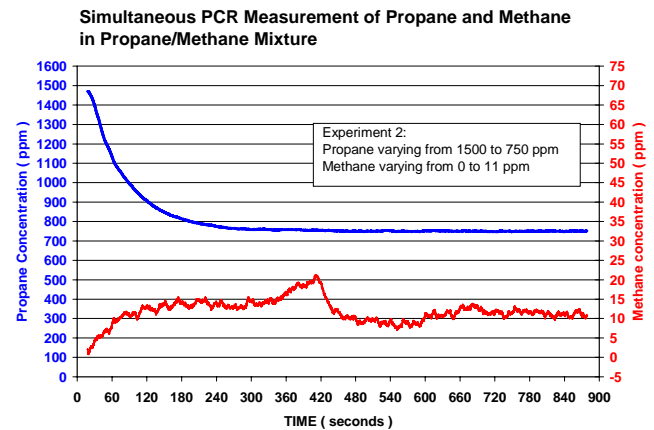


Fig. 4: Real-time calculation of methane and propane concentrations using the PCR methods. Refresh rate for instrumental response is 30x per second.

CONCLUSION

The Aspectrics, Inc. EP-IR spectrometer clearly demonstrated the capability of the technology to resolve spectrally overlapping chemical compounds in the gas phase for simultaneous quantitative analysis of both compounds.

In addition, the technology proved capable of quantifying a minor compound in solution in a spectrally overlapping major compound with accuracy at least equal to the precision of the reference method (gas blender setting.)

The combination of ruggedness of engineering and analytical capabilities of the EP-IR spectrometer promotes this analyzer as the ideal candidate for in-line simultaneous measurement of several chemical compounds in the gas phase, even if the relative concentrations are vastly different and if spectral overlapping occurs.