Simultaneous Measurement of Methane, Ethane and Propane in Gas Phase Using an Encoded Photometric InfraRed (EP-IR) Spectrometer.

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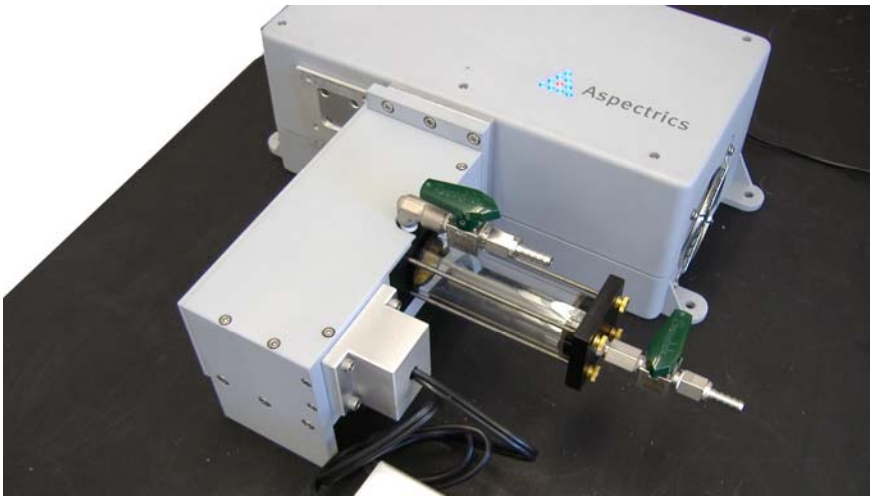

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SCOPE

This entire study was designed to prove the capacity of EPIR spectrometry to collect sufficient spectral information to enable the development of a multivariate quantitative analysis method for the simultaneous measurement of three hydrocarbon gases (methane, ethane and propane) in a mixture.

Moreover, this series of experiments were specifically designed to allow the modeling of a 1:1000 dilution of various concentrations of ethane and propane in a pure methane stream.

EXPERIMENTAL

SPECTROMETRY

Spectrometer: An Aspectrics MultiComponent analyzer (model MC5000A) was used for this analysis. Specifications for this analyzer are:

- 128 photometric channels
- Nominal spectral range: 2.5 – 5.0 microns (4000-2000 cm-1)
- 100 scans per second
- 60-second RMS noise @ maximum energy (~ 3.8 microns) less than 20 µAU (using an Aspectrics Verifier IR photometric testing fixture)

Gas Cell: An Aspectrics multipass I-Cell gas cell was used. Specifications are:

- Pathlength: 2.4 meters
- Internal Volume (excluding transfer lines): 100 mL
- Cell materials: glass body, calcium fluoride windows and gold coated mirrors.
- No temperature control on this model. All measurements were made at room temperature.

Data Collection: Parameters for data collection were:

- All data were collected using Aspectrics Commander™ data collection SW. It is to be noted that an ActiveX version of this data collection program exist, which ActiveX could be used for EPIR data collect from any ActiveX (MyInstrument Interface) compliant chemometrics software package.
- Boxcar setting of 6,000. This means that each spectrum collected results from the normalized co-addition of the previous 5,999 spectra and itself. From a practical viewpoint at a scanning speed of 100 scans per second, this translates into an actual integration time of 60 seconds (1 minute)
- Down Sample setting of 600. This means that only 1 in every 600 scans generated was actually saved. This corresponds to a response rate of the instrument of 1 new spectrum every 10 seconds.
- Gas sample data collection times.
    - In order to account for the time for the sample to fill the gas cell, a waiting time of 200-400 seconds was set between the collection of each sample in order to allow for stabilization of the gas mixture concentration in the gas cell and avoid sample carry-over contamination. It must be

noted that this delay time is strictly a function of the pneumatics design and is not a limitation of the instrument.

- In order to gather sufficient numbers of calibration, validation and prediction data points, 100 spectra or so were collected for each set of gas mixtures, requiring approximately 10 minutes doing so for each gas mixture.
- IMPORTANT NOTE: Aspectrics Commander™ software package allows controlling both the spectrometer for data collection and the Environics 4000 gas blender for delivery of samples. This level of automation allowed having all samples analyzed by a technician instead of tying up engineering and/or scientist time.

CALIBRATION, VALIDATION AND BLENDER PREDICTION SAMPLES

Calibration Standards:

- Only 7 calibration standards were used.
- These standards consisted of certified mixtures of methane, ethane and propane.
- Concentrations for ethane and propane ranged from 0 to 200 ppm (180 ppm effective after gas blender delivery due to MFC limitation) and 0 to 150 ppm (135 ppm effective after gas blender delivery due to MFC limitation), respectively.

  5 data points (mixtures) were created using orthogonal design (total lack of co-linearity between variations in ethane concentration and propane concentrations) in order to describe maximum variation with minimum number of standards.
- Concentrations of methane were the complement to 1000 ppm (900 ppm effective) in order to mimic a 1:1000 dilution of 0-20% ethane and 0-15% propane in a stream of pure methane.
- Spectra of monoblend methane, ethane and propane (diluted in dry nitrogen) were also added to the set of calibration standards.
- PRECISION OF REFERENCE METHOD: the use of certified mixtures of methane, ethane and propane allowed using only one Mass Flow Controller (MFC) at a time. This is important as the precision of the reference method for this calibration is that of the MFC of the gas blender: 1% relative to set concentration point according to Environics (gas blender manufacturer) published specifications.

Validation Standards:

- 5 validation standards were used.
- These standards consisted of certified mixtures of methane, ethane and propane.
- Concentrations for ethane and propane were carefully selected to be as different as possible from those in the set of calibration standards in order to test instrumental response linearity as well as accuracy in validation. Concentrations values ranged from 46 to 134 ppm for ethane and from 33 to 103 ppm for propane, while maintaining an orthogonal design to avoid co-linearity (still to describe maximum variation with minimum number of standards.)
- Concentrations of methane were the complement to 1000 ppm (900 ppm effective) in order to mimic a 1:1000 dilution of 4.6-13.4% ethane and 3.3-10.3% propane in a stream of pure methane.

- PRECISION OF REFERENCE METHOD: the use of certified mixtures of methane, ethane and propane allowed using only one Mass Flow Controller (MFC) at a time. This is important as the precision of the reference method for this calibration is that of the MFC of the gas blender: 1% relative to set concentration point according to Environics (gas blender manufacturer) published specifications.

Prediction Samples:

- 23 prediction samples were used, divided into two sets: (1) a set of 18 samples with all concentrations in methane, ethane and propane within the range for which the EP-IR had been calibrated; and (2) a set of 5 samples in which the methane concentration was deliberately set outside the range for which the instrument had been calibrated, while maintaining ethane and propane concentrations within the calibration concentration ranges.
- Initially, it was decided to generate random mixtures of methane, ethane and propane using three mono-blend tanks and a tank of dry nitrogen as solvent. However, such set-up would have required the use of 4 MFCs, each of which has a built-in precision (i.e. error) of 1% of set point.

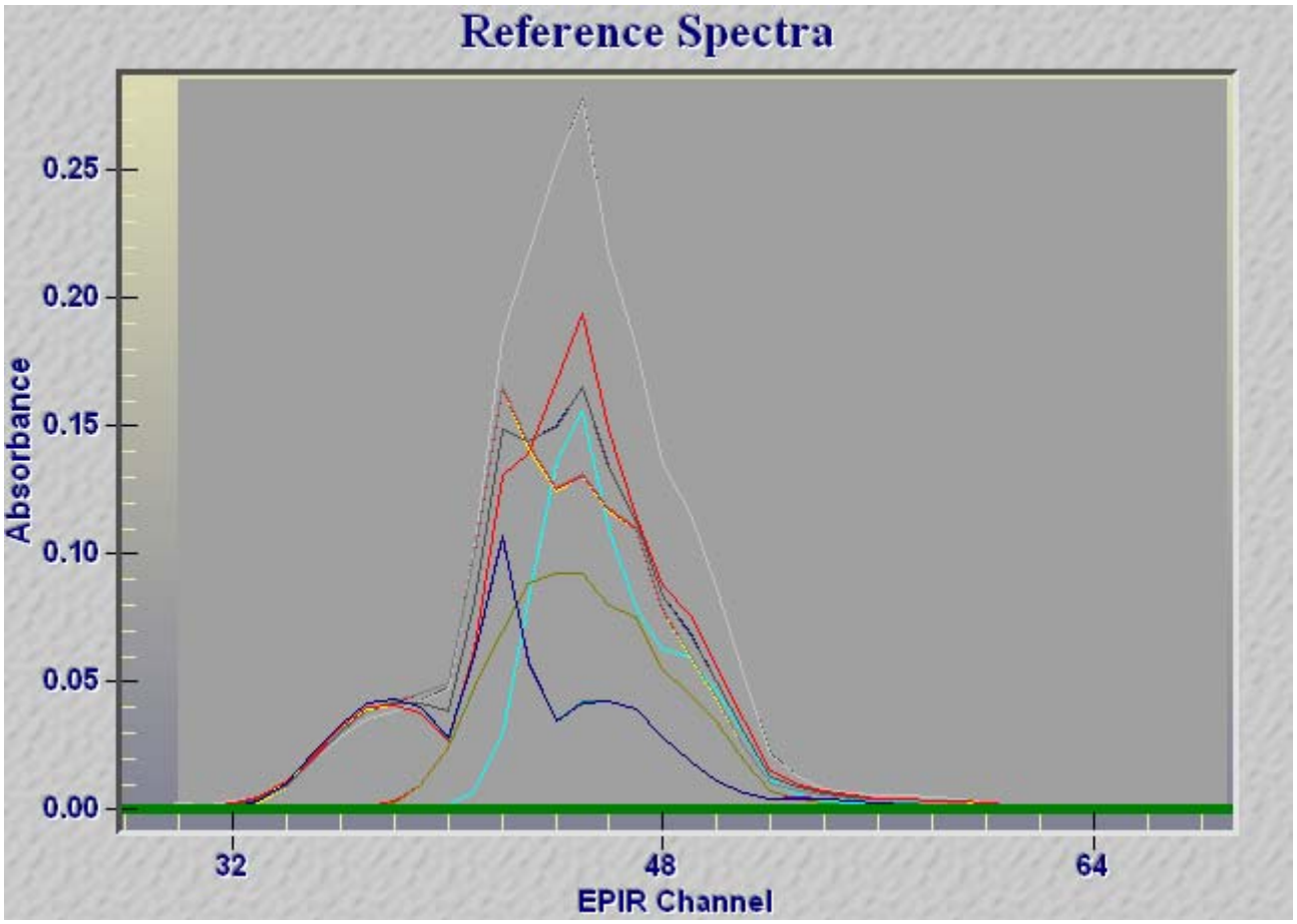
  In order to reduce the error on the reference measurement of each prediction blender sample, it was decided to use only 1 MFC for all zeros (dry nitrogen alone) and only 2 MFCs for the random mixture. This was accomplished by using one of the certified mixture tanks as solvent (carrier gas) and a second MFC allowing blending in some mono-blend gas. Since removal of co-linearity in sources of variations was not a focus in this prediction step, this solution was preferred as it allowed a smaller error on the reference measurement by using only 2 MFCs instead of 4 in the original experimental set-up
- PRECISION OF REFERENCE METHOD: the use of the above protocol allowed using no more than 2 MFCs at a time, each of which had a manufacturer specified precision of 1% relative to set concentration point. Considering the additive nature of errors of measurement, the precision of concentrations delivered by the gas blender was therefore kept at ± 2% relative to set point at most.

DATA TREATMENTS

- Aspectrics Chemobuilder™ chemometrics SW package was used to develop, optimize and validate the calibration equations as well as to predict the concentrations in the three gases in the gas blender mixtures.
- Quantitative algorithm used is Principal Component Analysis / Regression (PCA/PCR) applied onto automated polynomial baseline corrected absorbance spectra using dry nitrogen spectra as background.

RESULTS

CERTIFIED GAS MIXTURES CALIBRATION RESULTS (See Appendices A & B for detailed results)



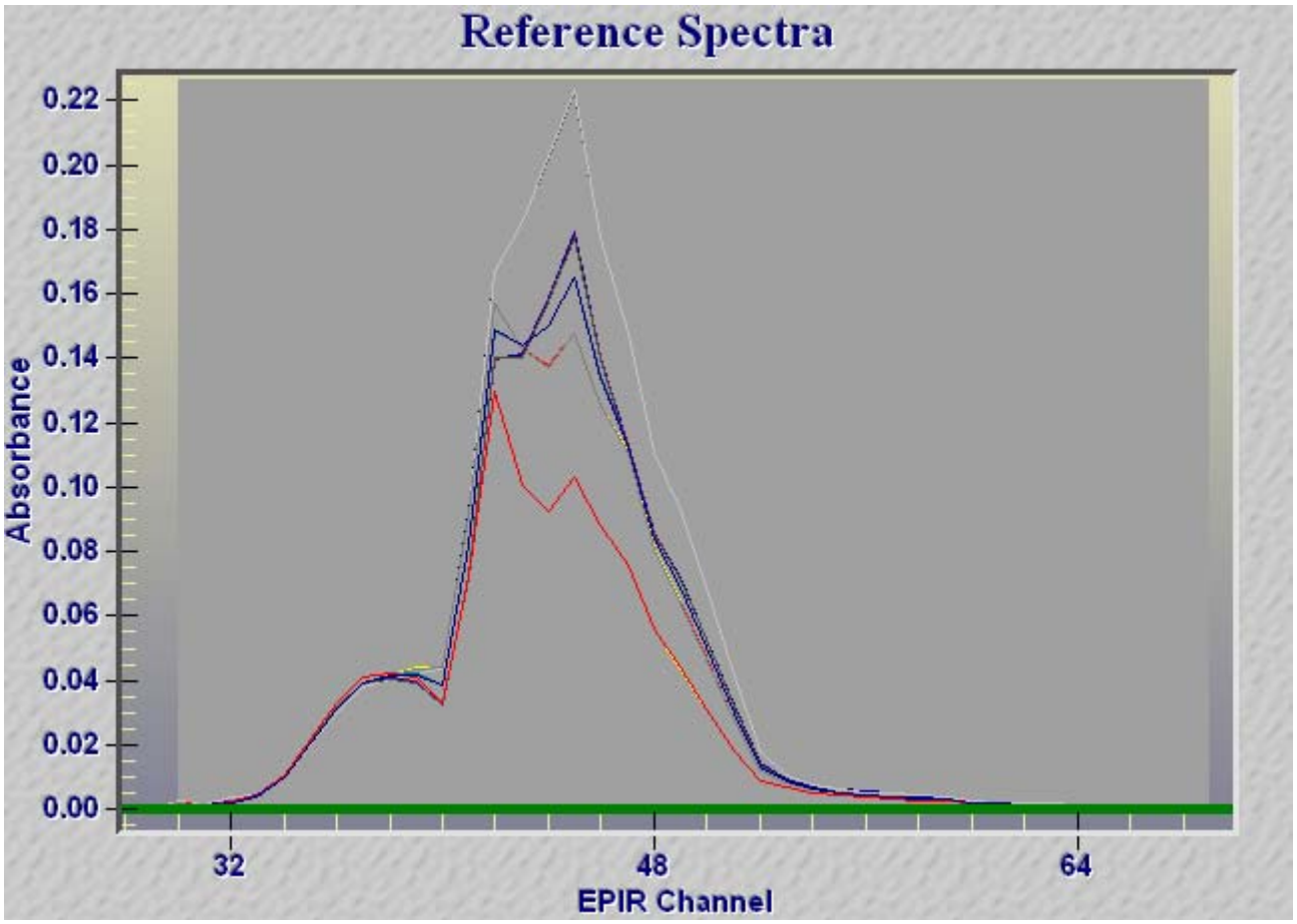
EPIR Calibration Standard Spectra – Zoom on 3.100 - 3.858 µm (2592.0 - 3225.8 cm^{-1})

		Methane	Ethane	Propane
Range	Min	584.00 ppm	89.96 ppm	67.65 ppm
	Max	900.00 ppm	180.13 ppm	135.00 ppm
	Avg	**743.00 ppm**	**157.43 ppm**	**118.00 ppm**
# spectra (*n*)		4,908	4,908	4,908

		Methane		Ethane		Propane	
		ppm	**% Rel.**	ppm	**% Rel.**	ppm	**% Rel.**
Accuracy (SEC)	1σ	0.99	**0.11%**	0.20	**0.11%**	0.43	**0.32%**
Precision	1σ	0.18	**0.02%**	0.03	**0.02%**	0.04	**0.03%**
LOD	1σ	0.64	**0.07%**	0.21	**0.12%**	0.23	**0.17%**

NOTE: % Rel. are relative to maximum concentration in range

CERTIFIED GAS MIXTURES VALIDATION RESULTS (See Appendices A & B for detailed results)



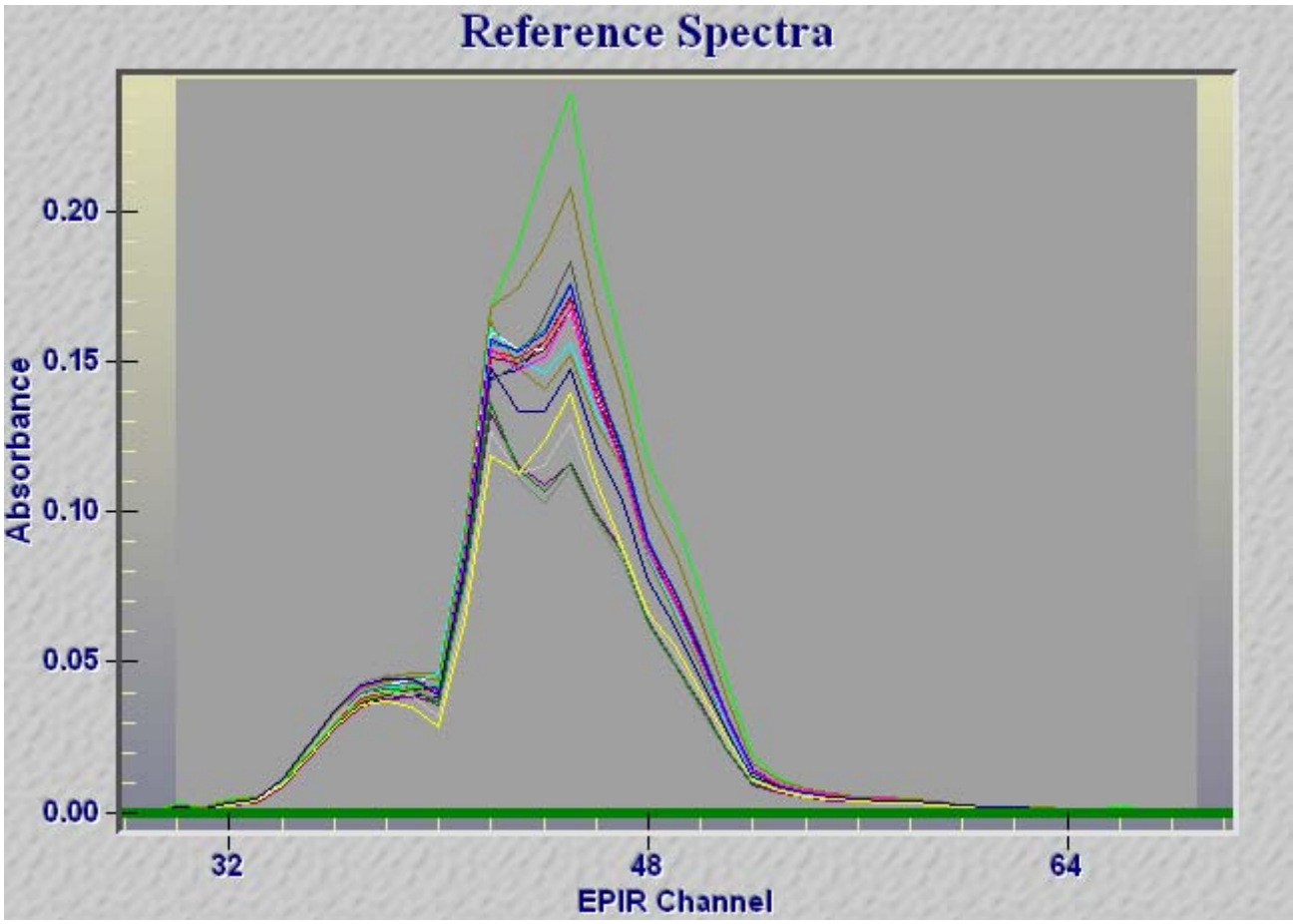
EPIR Validation Standard Spectra – Zoom on 3.100 - 3.858 µm (2592.0 - 3225.8 cm^{-1})

		Methane	Ethane	Propane
Range	Min	705.00 ppm	46.05 ppm	33.26 ppm
	Max	816.00 ppm	134.11 ppm	102.86 ppm
	Avg	**752.20 ppm**	**89.47 ppm**	**67.57 ppm**
# spectra (*n*)		3,505	3,505	3,505

		Methane		Ethane		Propane	
		ppm	**% Rel.**	ppm	**% Rel.**	ppm	**% Rel.**
Accuracy (SEP)	1σ	1.20	**0.16%**	0.39	**0.29%**	0.37	**0.36%**
Precision	1σ	0.28	**0.03%**	0.03	**0.02%**	0.04	**0.04%**
LOD	1σ	0.90	**0.11%**	0.31	**0.23%**	0.17	**0.17%**

NOTE: % Rel. are relative to maximum concentration in range

BLENDER GAS MIXTURES PREDICTION RESULTS (See Appendices A & B for detailed results)



EPIR Prediction Sample Spectra – Zoom on 3.100 - 3.858 µm (2592.0 - 3225.8 cm^{-1})

		Methane		Ethane		Propane	
Range	Min	644.29 ppm		33.40 ppm		24.77 ppm	
	Max	820.80 ppm		158.92 ppm		118.11 ppm	
	Avg	**731.89 ppm**		**98.87 ppm**		**61.11 ppm**	
# spectra (*n*)		3,505		3,505		3,505	
		ppm	**% Rel.**	ppm	**% Rel.**	ppm	**% Rel.**
Accuracy (SEP)	1σ	9.62	**1.17%**	1.49	**0.94%**	0.69	**0.58%**
Precision	1σ	0.42	**0.05%**	0.05	**0.03%**	0.07	**0.06%**
LOD	1σ	0.22	**0.03%**	0.07	**0.04%**	0.09	**0.08%**
Est. Blender Error (1σ) 1% of set point * 2 MFCs		14.64 ppm		1.98 ppm		1.22 ppm	
Calib. Method Error (1σ)		1.39 ppm		0.57 ppm		0.49 ppm	
Total Expected Measurement Error (1 σ)		**± 16.03 ppm**		**± 2.55 ppm**		**± 1.71 ppm**	

NOTE: % Rel. are relative to maximum concentration in range

CONCLUSION

The EP-IR MC5000A delivered excellent analytical results in calibration and validation for the simultaneous measurement of methane, ethane and propane in gas phase.

Most impressive are the precision values obtained for all measurements, whether analyzing calibration, validation of gas blender prediction samples. As a matter of fact, accuracy calculations depend on the precision of the Mass Flow Controllers used in the gas blender (1% relative to set concentration point according to the manufacturer). Evaluating EP-IR spectrometric performance on the precision of the chemometrics output provides a better appreciation of the technique as applied to gas analysis (according to the manufacturer, MFCs have a specified precision of < 0.5% relative to set point).

With these qualifications in mind, we observe that:

(1) The chemometrics methods are accurate. Using an orthogonal experimental design and certified gas mixtures to minimize reference method precision errors, a very accurate model was developed, characterized by 1*σ (RM)SEC for all compounds of less than 0.32% relative to maximum concentration in the range of calibration standards, and by 1*σ (RM)SEP for all compounds of less than 0.36% relative to maximum concentration in the range of validation standards.

(2) The chemometrics methods are precise. The analytical (chemometrics) outputs provided by the PCR quantitative model proved to be remarkably repeatable, with precision never exceeding 0.11% relative to average concentration in the range, regardless of the nature of the gas sample.

(3) The chemometrics methods provide very low LOD measurements. LODs (calculated as 1σ accuracy for all gas concentrations equal to zero) also proved remarkably low, never to exceed 0.23% relative to the maximum range concentration in the set of spectra.

(4) The chemometrics methods provide no false positive response. Analysis of samples with only 2 or 1 of the three gases showed that no false positive could be observed with the quantitative multivariate model created in this study.

This experiment proves the capacity of EP-IR to provide adequate spectral information to model the simultaneous measurement of methane, ethane and propane in conditions mimicking the presence of ethane and propane in pure stream of methane.