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DETERMINATION OF THE COMPOSITION AND THE GROSS HEATING VALUE OF A MIXTURE OF GASES BY INFRARED SPECTROSCOPY AND CHEMOMETRIC METHODS

N.Makhoukhi

FRANCE

ABSTRACT

The composition and the GHV (gross heating value) of a mixture of gases are of prime concern to the operators of transmission lines, distributors, and large industrial users. They must be accurately determined at all major custody transfer points. The accuracy and the availability of detailed composition information from chromatographic procedures make them very useful but they are time consuming, expensive and not well adapted to on-line (real-time) measurements. In this paper, we present the results of a chemometric analysis in the mid and near-infrared range for a gas mixture, with a composition close to that of natural gas. The goal of our work is to propose a quantitative infrared measurement of chemical composition and GHV for gaseous mixtures such as natural gas, at atmospheric pressure and ambient temperature, suitable as an alternative to chromatographic analysis. Therefore, our techniques have been developed on synthetic mixtures of methane, ethane and propane, which are the major components of natural gas. IR spectra and chemometrics processing are used to determine the concentrations of the three gases and the GHV of their mixtures. Two spectral ranges mid (MIR) and near-infrared (NIR) and two multicomponent methods PLS (Partial Least Squares) and PCR (Principal Component Regression) have been tested to achieve the best estimation of the concentration and the GHV. Finally, our method has been directly tested with a natural gas sample taken from a pipeline.

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1. PREAMBLE

Spectroscopy provides an alternative to the existing techniques for process control applications in general [1]. Thus, the infrared region is ideal for analysis of a gaseous mixture because the IR spectroscopy offers an abundance of chemical informations [2]. Moreover, it is a non-destructive method and the spectra can be acquired rapidly, making on-line measurement easier. The individual component concentrations in gaseous mixture can be determined, even in a complex matrix, by using chemometric processing [3]. The GHV can be determined starting from composition of the gaseous mixture or directly by infrared spectroscopy. Our study was elaborated in the laboratory with the aim of on-line application [4].

2. EXPERIMENTAL

2.1 Samples

The mixtures of methane, ethane and propane were prepared in the laboratory. The experimental arrangement used in the preparation was based on the calculation of partial pressure of each component. The total pressure was 5 bars. In order to reduce the number of samples and to obtain a good prediction, the choice of representative samples was done from an experimental design theory [5]. Thirty three mixtures were prepared with the percentage composition of CH_4 varying between 86 and 95 mol%, C_2H_6 between 2 and 10 mol%, and C_3H_8 between 0 and 4%. The reference compositions were determined by gas chromatography and used to build calibration model.

2.2 Apparatus

Spectra were collected for all samples, at different resolutions, i.e 0.25, 0.5, 1, 2, 4, 8 cm^{-1}. The gas cell was built by us from stainless steel. The effective pathlength of the gas cell used for NIR measurement was 106 mm. For the MIR measurement, the pathlength was 18 mm. CaF_2 cell windows were used in both spectral ranges.
The spectra were collected at 1 bar for NIR and 0.3 bar for the MIR. In all cases, we worked under ambient temperature and the background was recorded with the cell under vacuum.
Principal component regression, PCR, and partial least squares, PLS, analyses were performed using Turbo Quant software by Nicolet Inc [6].

3. RESULTS AND DISCUSSION

3.1 Qualitative analysis and spectral area

The mid and near-infrared spectra of pure methane, ethane, and propane are presented in figures 1 and 2. We observed that the bands of the three gases are strongly overlapped. In this case, PLS and PCR methods must be used to find the component composition.
Figure 1 shows that in the mid-infrared spectrum of the mixture, two distinct regions which are useful for extracting quantitative information. The first one is the C-H bending region [1204-1390 cm^{-1}], and the second [2818-3181cm^{-1}] covers the C-H stretching modes.
Figure 2 shows four special ranges in the near-IR spectra of mixture. The ranges 4070 to 4650 cm^{-1} and 7010-7670 cm^{-1} correspond to the first and second C-H combination bands, respectively. The ranges 5490-6160 cm^{-1} and 8430-8950 cm^{-1} correspond to the first and the second harmonics, respectively [7].

3.2 Optimisation of calibration models

We tested five varying parameters which are: spectral resolution, spectral area, spectral domain, spectral pre-treatment, regression methods to achieve the best estimation of the concentration and the GHV. After model optimisation, our method is directly evaluated with natural gas as sample.
Before calibration, a spectrum outlier diagnosis was carried out to find the spectra of the standards which are most different from the spectra of the other standards using either the Dixon or the Chauvenet test for outliers to determine whether is significant the difference. Thus, the diagnosis

makes it possible to eliminate the spectra which present either : acquisition or handling problems for each calibration sample.

For all tests, the number of model factors is optimized in order to obtain the best calibration. The calibration errors were estimated from the RMSECV (Root Mean Square Error of Cross-Validation) for the cross validation from 22 synthetic gaseous mixture (m). The RMSEP (Root Mean Square Error of Prediction) was estimated for 9 synthetic gaseous mixtures (n).

$$RMSECV = \sqrt{\frac{\sum_{j=1}^{m}(y_j - y'_j)^2}{m-1-q}}$$

$$RMSEP = \sqrt{\frac{\sum_{j=1}^{m}(y_j - y'_j)^2}{n}}$$

Where y_j and y'_j correspond respectively to the reference and predicted composition for the component j and q is the number of factors used to build calibration model.

For each varying parameter to study we carried out a cross validation, giving a value of RMSECV, which represents at the same time a criterion on the calibration and the prediction according to its definition. Among the models obtained, we retained those corresponding to the best RMSECV, which lies between the minimal value of the RMSECV (RMSECV$_{min}$) and RMSECV$_{min}$+Є, where Є corresponds to the uncertainty of the method of reference. Here it is worth 0,1% for the composition and 0.06 kWh/m^3 for the gross heating value (CPG). We tested these models on a whole of sample tests. We retain that corresponding to the minimal value of the RMSEP.

According to our methodology of optimization, we find the following results:

The best model for the determination of the composition by infrared spectroscopy was obtained for the following parameters:

-Spectral domain: Near-Infrared
-Regression method: PLS
-Spectral resolution: 2 cm^{-1}
-Spectral area : 4079-4644, 5484-6164 et 7017-7670 cm^{-1} for CH_4, 4079-4644, 5484-6164 et 8429-8941 cm^{-1} for C_2H_6 and 5484-6164 cm^{-1} for C_3H_8.
-Spectral pre-treatment : first derivative D1.

The best model for the direct determination of the gross heating value by infrared spectroscopy was obtained for the following parameters:

-Spectral domain : Near-Infrared
-Regression method : PLS
-Spectral resolution : 2 cm^{-1}
-Spectral area : 4079-4644cm^{-1}.
-Spectral pre-treatment : Standard Normal Variate SNV.

3.3 Prediction for natural gas sample

The composition and the Gross Heating Value (GHV) of four natural gas samples taken from a pipeline were predicted with the calibration methods presented above for synthetic gases. The composition of the samples was determined first by gas chromatography. To find the composition and the Gross Heating Value by PLS analysis in the near-infrared, we used the same experimental conditions defined previously for calibration samples. Table 1 compares the percentage compositions of the three gases for the four samples, obtained both by gas chromatography and infrared method and the GHV determined from the composition by the two methods. Table 2 compares the GHV determined directly from infrared spectra to those determined indirectly by gas chromatography. For the composition the error is small for methane, acceptable for ethane and important for propane. For this latter, this is due to its lower concentration in the mixture. On the other hand, we note that

methane and the propane are overestimated. All the errors can be explained by the presence of higher hydrocarbons (C_4 and greater) present in natural gas.

We observed that the gross heating value seems better determined indirectly from the prediction of the natural gas composition than from a direct estimation. This can be easily explained by the fact that the reference value is indirectly obtained by the gas chromatography method and not from a calorimetric method.

4. CONCLUSION

The results show that the NIR range is more suitable than MIR range for gas analysis. The use of the PLS method is also better than the PCR method for gas spectral data. A near infrared spectrometer with a resolution of 2 cm^{-1} for the spectral regions selected is shown to be a good alternative to gas chromatography for determining the composition and the gross heating value of natural gas. Optical-fiber measurements coupled with near-infrared spectra can be used for remotely monitoring the energy content and the composition of natural gas *in situ*. Developments and implementations of infrared spectroscopic techniques is thus a logical step forward for processes monitoring in the gas industry.

5. REFERENCES

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Table 2: Chromatographic results and PLS natural gas gross heating value prediction in the near-infrared.

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Fig 2 : NIR spectra of pure gases at 0.5 cm^{-1} resolution.

sample	GNGSO1		GNGSO2	
composition	GC	NIR	GC	NIR
methane	91.286	93.042	93.218	95.314
ethane	5.384	5.734	3.402	3.784
propane	0.870	1.428	0.554	0.991
GHV (kWh/m^3)	11.519	11.513	11.230	11.359

sample	GNGSO3		GNGSO4	
composition	GC	NIR	GC	NIR
methane	88.838	91.517	90.531	93.156
ethane	6.713	6.453	5.309	5.186
propane	1.272	1.700	0.947	1.415
GHV (kWh/m^3)	11.665	11.684	11.469	11.538

Table 1 : Chromatographic results and PLS natural gas compositions prediction in the near-infrared and GHV determined from the composition.

	GHV (kWh/m^3)		
samples	GC	NIR	difference
GNGSO1	11.519	11.675	**0.156**
GNGSO2	11.230	11.541	**0.311**
GNGSO3	11.665	11.750	**0.085**
GNGSO4	11.469	11.628	**0.159**

Table 2 : Chromatographic results and PLS natural gas gross heating value prediction in the near-infrared.

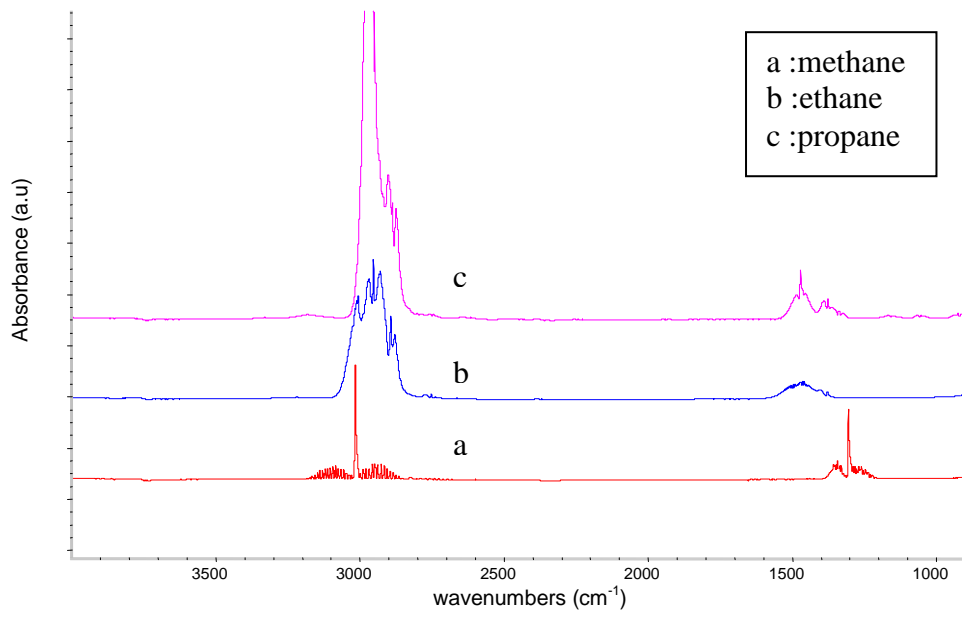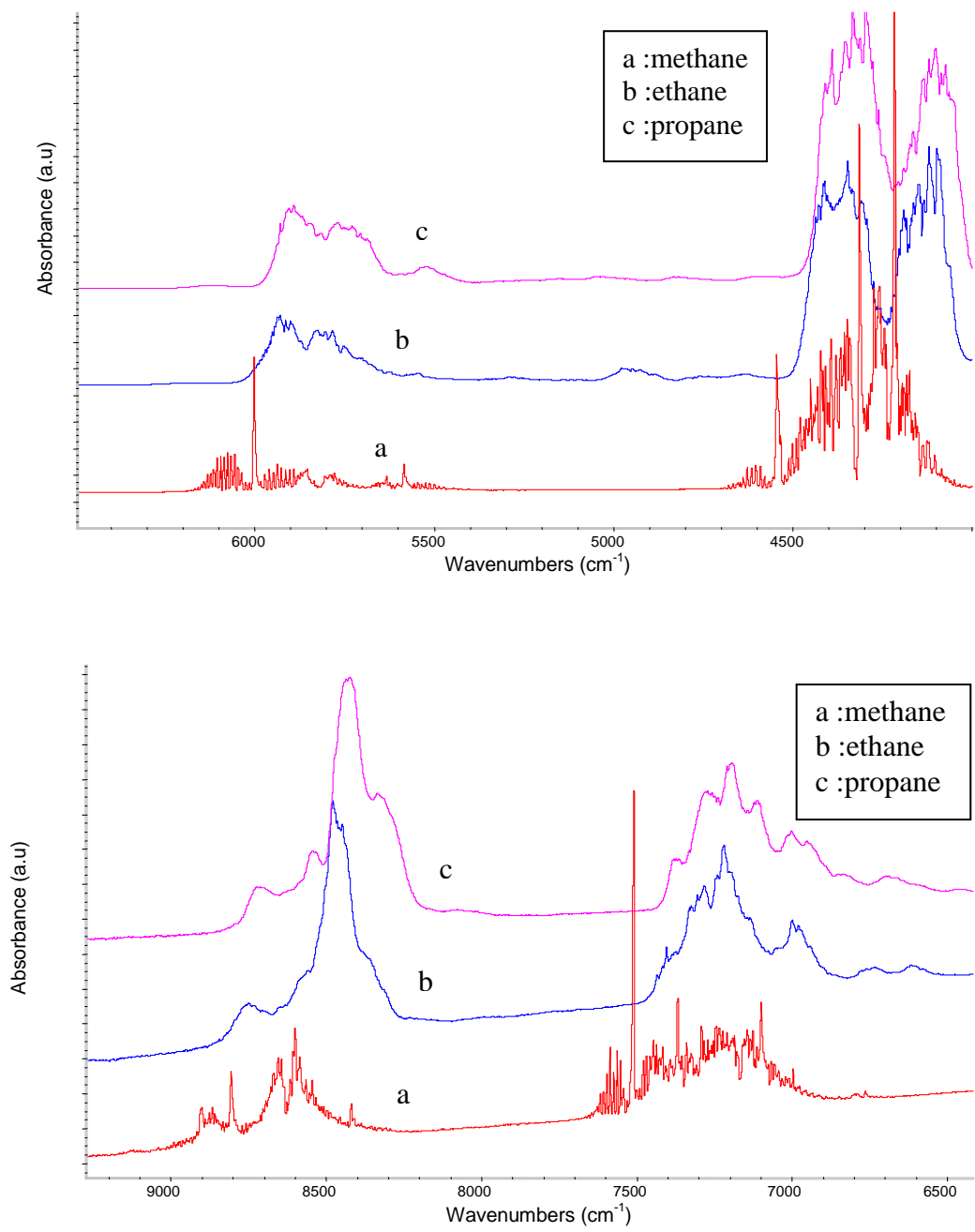Fig.1 : MIR spectra of pure gases at 4cm^{-1} resolution.

Fig. 2 : NIR spectra of pure gases at 4 cm^{-1} resolution