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THE SPECTRUM LENGTH METHOD IN QUANTITATIVE INTERPRETATION OF SELECTED OPTICAL SPECTRA

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Abstract. *Different algorithms are used for the quantitative interpretation of optical spectra. Regression methods e.g CLS (Classical Least Squares) or PLS (Partial Least Squares) are often used in typical problems of laboratory spectroscopy. The spectra analysis is generally a multi-step process, in which, depending on the spectra type, modification of individual regression methods or special dedicated methods are applied. For example, contour length method or spectra length algorithm are used in this purpose. The basic version of the algorithm is very simple in terms of mathematics. It has been proposed for the analysis of spectra in the OP-FTIR open path spectroscopy, where there are significant fluctuations in the spectrum baseline. The spectrum length is a parameter closely related to the content of the analyzed gas component. Independently of spectral length algorithm, a method has been developed in which difference length of two spectra (measured and reference) is used to compare the spectra. The minimum length of the spectral difference is an indicator of their best fitting. The article presents two ways of using the spectrum length: as a direct and indirect parameter indicating the measured quantity on the basis of the spectrum. There were performed the spectrum length algorithm as a digital differentiating filter with a specific frequency response. There were also analyzed more advanced differentiating filter and the possibility of frequency spectrum filter design used in an analysis of optical spectral signal. There were performed the analysis of the spectrum length method in the case of the synthetic calibration involving the use of model spectra from simulations realized by HITRAN database. There were analyzed numerically the problem of the Instrument Line Shape influence on the synthetic spectra and results of the determining the content of components by the minimizing the difference of spectral length.*

Keywords: OP-FTIR, optical spectra, quantitative analysis, digital differentiating filter

METODA DŁUGOŚCI WIDMA W ILOŚCIOWEJ INTERPRETACJI WYBRANYCH WIDM OPTYCZNYCH

Streszczenie *Do ilościowej interpretacji widm optycznych wykorzystuje się wiele różnych algorytmów. W typowych zagadnieniach spektroskopii laboratoryjnej wykorzystuje się m. in. metody regresji CLS, PCR PLS. Interpretacja widm to często proces wieloetapowy, w którym w zależności od rodzaju widm wykorzystuje się modyfikację poszczególnych metod regresji lub też stosuje się specjalne metody dedykowane. Jedną z takich metod jest algorytm długości konturu lub też długości widma. Jego podstawowa wersja jest bardzo prosta pod względem matematycznym. Została zaproponowana do analizy widm ze spektroskopii otwartej ścieżki OP-FTIR, dla której występują znaczące fluktuacje linii bazowej widma. Długość widma jest parametrem, który jest odwzorowany bezpośrednio na zawartość danego składnika gazowego. Niezależnie od algorytmu długości widma powstała metoda, w której długość różnicy dwóch widm (mierzonego i odniesienia) służy do porównania widm. Minimalna długość różnicy widm jest wskaźnikiem ich najlepszego dopasowania. W pracy porównane zostaną obydwa sposoby wykorzystania długości widma: jako parametru bezpośrednio lub pośrednio wskazującego wielkość poszukiwaną na podstawie widma. Przeanalizowany zostanie algorytm długości widma jako cyfrowy filtr różniczkujący posiadający określoną charakterystykę częstotliwościową. Przeanalizowane zostanie zagadnienie wykorzystania bardziej zaawansowanego filtru różniczkującego oraz możliwość uwzględnienia w wyborze i projektowaniu filtra widma częstotliwościowego optycznego sygnału spektralnego. Kolejno poruszanym zagadnieniem będzie analiza metody długości widma w przypadku tzw. kalibracji syntetycznej polegającej na wykorzystaniu jako widm wzorcowych widm pochodzących z symulacji wykorzystujących bazę danych Hitran. Przeanalizowany numerycznie zostanie problem wpływu kształtu odpowiedzi instrumentu pomiarowego na syntetyczne widma i wyniki wyznaczania zawartości składników metodą minimalizacji długości różnicy widm.*

Słowa kluczowe: OP-FTIR, widma optyczne, ilościowa analiza, cyfrowe filtry różniczkujące

Introduction

Optical data can be measured in different ways. The optical spectra measurement can be processed in laboratory or *in situ*. Some kinds of industry require to conduct measurements from a distance of atmospheric gases or gas products of chemical reaction e.g outlet gases from as a product of combustion of biogas [4]. In the context of sustainable urban design, measurements of atmospheric gas, in particular greenhouse gases are crucial [8]. The open path Fourier Transform Infrared Spectroscopy (OP-FTIR) is a method using in situ measurements. The main advantages of this method are: non-invasive measurements, possibility of simultaneous measurement of many components (the entire spectral range of the spectrum is determined in one measurement act), simple measuring system, quick process of conducting measurements and no necessity of preparing samples for analysis [12]. Additionally, OP-FTIR spectrometer enables measurements in difficult weather condition, where there may be high temperature and high dust level [13].

Due to unstable measuring conditions, e.g. non-constant temperature, frequent changes of the reference spectrum, interference from water vapor and carbon dioxide, the data from OP-FTIR spectrometer is not suitable for direct qualitative or quantitative analysis. The second major problem in the context of optical spectral preprocessing is background spectra measurements. In order to calculate the content of the spectrum component, there is a need a knowledge of a sample single-beam spectrum and background spectrum without spectrum of the analyzed compound [11]. Background spectrum measurement is very complicated or even not possible to conduct (e.g the atmospheric gas measurements). For these reasons obtained measurement spectrum require implementation of advanced spectrum processing techniques.

1. Quantitative analysis in OP-FTIR

The conducting of a spectra quantitative analysis is mainly aimed at construction a mathematical model on the basis of which it will be possible to determine the content of a selected substance in the spectrum. The construction of such a calibration model allows to avoid additional costs and save time as a result of carrying out subsequent measurements. In this regard, various methods of regression analysis are used, e.g. regression of principal components PCR (Principal Component Regression), partial least squares regression PLS (Partial Least Square Regression) and multiple linear regression MLR (Multi-linear Regression) [7, 14].

Due to the characteristics of the OP-FTIR spectrometer measurement data, in some cases it is not possible to perform a direct calibration. It caused the development an alternative methods as a quantitative analysis of optical spectra. For reference spectrum measurements issue, there were developed quantitative methods for measuring analyte concentrations, for instance spectral subtraction method of gas phase FTIR [10] and a single beam titration method [16]. It was developed the spectrum length method applied in gas concentration analysis [1] and was successfully implemented in the context of quantitative analysis of spectra measured by TFBG (Tilted fiber Bragg grating) [6].

As concerns the spectrum analysis with any parameters, spectral features modelling with mathematical methods are applied. For this purpose, simulation spectra are most often used, available e.g in the HITRAN database [9]. The influence of temperature on OP-FTIR spectra quantitative analysis is very significant and complicates conducting an appropriate model calibration [5]. For high temperature measurements there is a need to use a dedicated HITEMP database [15].

2. Materials and experimental methods

2.1. Data description

The analysis was performed on the basis of synthetic data and measured data. The simulation spectra have been modelled in accordance with HITRAN database [9] and there were conducted modelling of carbon (II) oxide spectra (CO) for different concentrations (2.5%, 5%, 10%, 20%, 25%, 33% and 50%). The analysis of calibration spectra was conduct using the calibration spectra of CO [2] and methan (CH_4) [3]. The calibration for two gases CO and CH4 was also performed for different concentration. The conditions for the gases calibration were as follows: path length was 10 cm, the spectra were collected at 4 cm^{-1} resolution [2, 3]. The concentrations for CO gas was as below: 2.5%, 5%, 10%, 20%, 25%, 33% and 50% [2] and for CH_4 gas: 2%, 5%, 7%, 10%, 20%, 30%, 40%, 50%, 60%, 70% [3].

2.2. Methods applied

The algorithm which was applied in this experimental has been developed in MATLAB.

In order perform the quantitative analysis of spectra for different concentrations there were applied a spectrum length method (SLM) , which was based on a very simple idea. The main goal of this method is compute the spectrum length by summing up the differences between two adjacent points of analyzed spectrum [1].

The length of absorbance spectrum, which contains N points can be obtained by formula below:

$$L = \sum_{i=0}^{N-1} |A_{i+1} - A_i| \quad (1)$$

where A is the absorbance of spectrum [1]. The difference between two points of spectrum can be received by subtracting absorbance values from two adjacent points. However, digital differentiating filters may be used as a spectrum length algorithm. In this paper, there were designed several digital differentiating filters depending on the frequency spectrum of optical spectral signal.

2.3. Digital differentiating filter designing

Before the designing of digital differentiating filters, there were computed the frequency spectrum of selected optical spectra by using FFT (Fast Fourier Transform), which computes the DFT (Discrete Fourier Transform). This procedure was conducted with the aim to define the frequency ranges with useful information and the others ranges with unwanted signal e.g. signal noise.

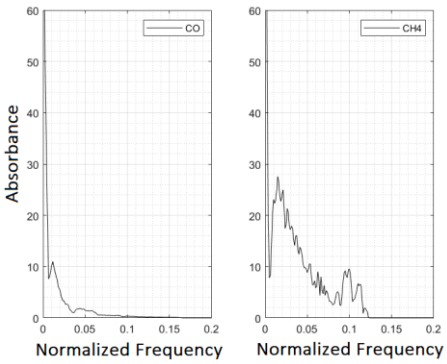

Fig. 1. Frequency spectrum of CH4 spectra and CO spectra

Based on received frequency spectrum of two gases (Fig. 1), the frequency ranges necessary for the design of differential filters were obtained. In the case of the CH_4 spectra, there were observed the useful information in the range 0-0.2 frequency and for the CO spectra is the range 0-0.1 frequency. For this reason, it was important to design differentiating filters, which will attenuate signal out of defined ranges with information.

With the aim to conduct optimal signal filtration, there were used built-in functions in MATLAB. Three types of filters were selected. Firstly, the Savizty-Golay filter was applied, where there were selected seventh filter order. With using the function *firpm* the Parks-McClellan FIR differential filter was designed. It was selected the 30th order of filter. The Least-square linear-phase FIR filter with 15th filter order was designed based on the *firls* function. Fig. 2 presents the frequency response of designed filters.

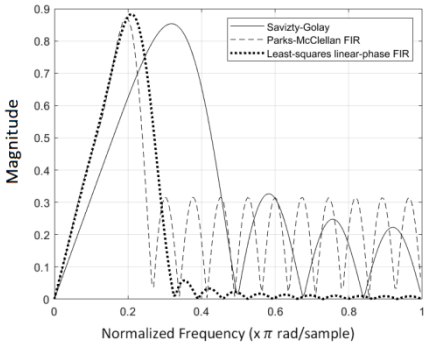

Fig. 2. Frequency response of selected digital filters

In the next step of spectrum processing, there were used constructed digital filters in order to compute the differential of the gas spectra as a SLM procedure. The spectra differentiation was performed on the preprocessing data (e.g. selection of wavenumber ranges with characteristic peaks of analyzed gas). In the final processing step, the contour spectra length was calculated. As an example there were presented the differential of spectra of 50% concentration CO obtained by Savizty-Golay filter.

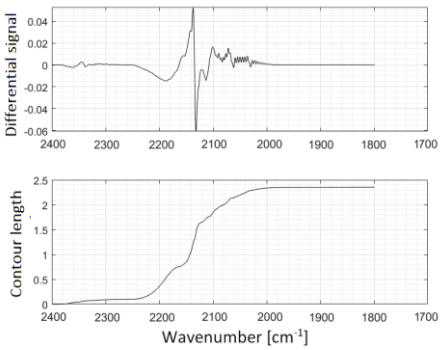

Fig.3. The differential signal and contour length for CO spectra

To perform the SLM procedure, there were selected three types of digital differential filters to demonstrate the difference between them. The two calibration spectra (CO and CH_4) was processed by using the same types of digital differential filters.

2.4. SLM procedure with synthetic spectra

On the base of HITRAN database, there were calculated synthetic spectra using by line-by line method. The CO synthetic spectra was selected with different concentrations (as the same in the case of calibration spectra). It was computed the proper Instrument Line Shape (ILS) function with measurement resolution 4 cm^{-1}. The data loading and processing also was supported by MATLAB. In the next step, it was added to synthetic spectra the modeled errors representing the signal noise

and inappropriate ILS distortion. This process was performed to demonstrate the SLM procedure as a parameter to evaluate of modeling synthetic spectra.

Additionally, there were designed the Difference Length Spectrum (DLS) parameter to evaluate the ILS function adjustment. The algorithm of DLS parameter was based on calculation of difference between analyzed contour length (CL_a) and ideal contour length (CL_i) with correct parameters. The algorithm of DLS parameter was based on formulas below:

$$DLS(w) = CL_a - CL_i \quad (2)$$

DLS parameter was described as a function of wavenumber (w). In the next step, there were calculated a derivative of $DLS(w)$ and *NDLS* (Normalized Difference Length Spectrum):

$$NDLS(w) = \frac{|DLS'(w)|}{\max(|DLS'(w)|)} \quad (3)$$

The optimal synthetic calibration result is obtained by the minimum of *NDLS*.

3. Results

In this section there were presented the results of SLM procedure in the case of concentrations analysis of calibration spectra and of evaluation correct synthetic spectra modeling.

3.1. Calibration spectra

There were processed three types of digital differential filters in SLM procedure. As the results there were obtained charts presents the contour length spectra as an analysis of gas concentrations of CO and CH_4. Fig. 4 and Fig. 5 presents the implementation results of SLM procedure to determine gas concentrations for CO and CH_4 spectra.

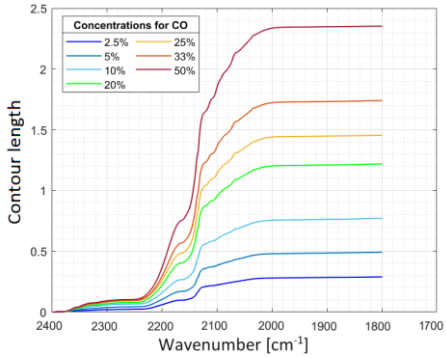

Fig. 4. SLM procedure with Savizty-Golay filter. CO calibration spectra

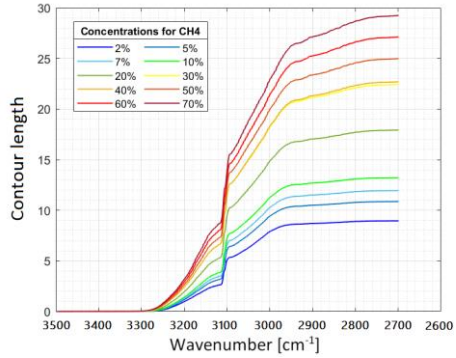

Fig. 5. SLM procedure with Least-square linear-phase FIR filter. CH_4 calibration spectra

The received contour length results could be used to support interpretation of gas content in the case of input spectra data with fluctuating baselines. There is possibility to distinguish the concentrations values of analyzed gases.

In order to compare three filters applied, there were obtained max values of contour length method for each gases. The Fig. 6 and Fig. 7 shows the differences between DDF applied.

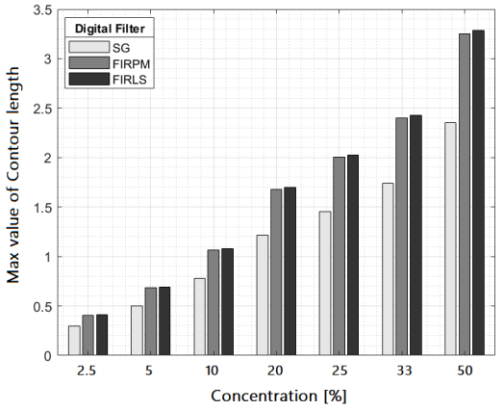

Fig. 6. The differences between three types of DDF. CO Calibration spectra

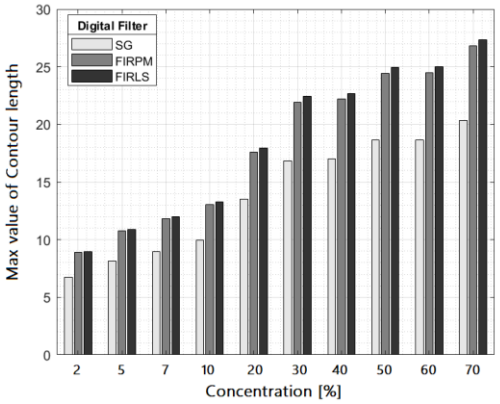

Fig. 7. The differences between three types of DDF. CH_4 Calibration spectra

Based on the obtained results of three types of DDF, there were observed the lowest value of contour length in the case of CO spectra and CH_4 spectra. Additionally, the highest values were presented by the same DDF least square linear phase FIR in both cases of spectra.

3.2. Synthetic spectra

SLM procedure was used in processing of modelling synthetic spectra as parameter to determine the simulation spectra quality. In the first case, there were modelled signal noise and added to analyzed synthetic spectra to illustrate the SLM sensitivity to added noise.

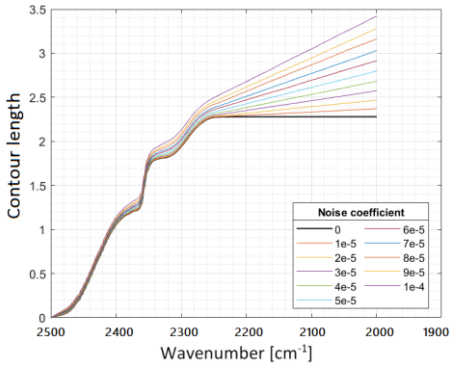

Fig. 8. Influence of adding signal noise to SLM results

Fig. 8 presents the significant influence of signal noise with small coefficient. The SLM procedure has a high sensitivity to noise signal.

In the second case, there were considered the influence of spectrometer measurement resolution to ILS function, which is selected during simulation synthetic spectra in order to modelled influence of measuring instrument.

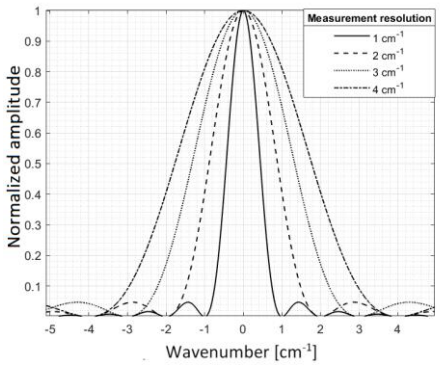

Fig. 9. Measurement resolution influence on ILS function

The Fig. 10 describes the impact of inappropriate ILS function on SLM results. The contour length spectra obtained by selected measurements resolution presents significant differences, which are caused by selection small measurement resolution range. Therefore, there is a need to make property selection of ILS function to calculate correctly simulation synthetic spectra.

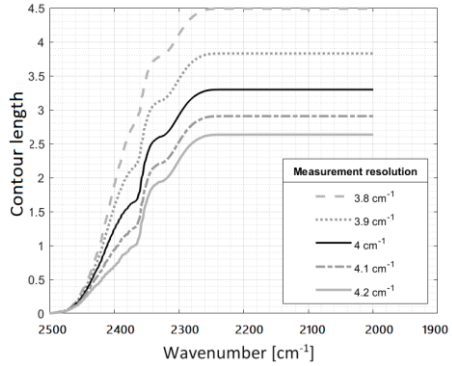

Fig. 10. Measurement resolution influence on SLM results

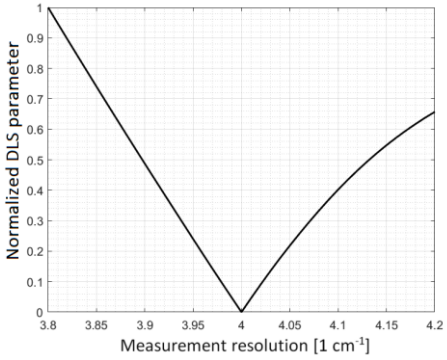

Fig. 11. NDLS parameter results

The *NDLS* parameter was designed to support the correct selection of measurement resolution (Fig. 11). The lowest value of *NDLS* parameter indicate the best adjustment of ILS functions. To demonstrate the NLDS operation, the 4 cm^{-1} measurement value was taken as a reference value.

4. Summary

The spectrum length method as a quantitative analysis method of optical spectra meets the assumptions. There were processed the gas concentrations analysis by using different digital filters. The method is fast and very simple to implement. Regard to possibility of many filters selection, the SLM procedure could be matched to several kinds of input data. It worth to point out, that due to the reduction of computational complexity, the DDF with the lowest filter order are desirable. On the other hand, the processing SLM with synthetic spectra demonstrated inadequacies of this method in the case of spectra with signal noise or inappropriate ILS function. For this reason, further research will be focus on development SLM procedure, which will be not sensitivity to noise signal and imperfect ILS model.

Acknowledgments

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