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Influence of gas concentration inhomogeneity on measurement accuracy in absorption spectroscopy

Abstract. The article presents influence of a variable compound concentration along measurement path on results obtained by absorption spectroscopy. It is very important, especially for the case when long optical path are applied. The discussed measurement method is utilized e.g. in environment control of power boilers when biomass is co-combusted with coal.

Streszczenie. Artykuł porusza problem wpływu na wynik pomiarów uzyskanych metodą spektroskopii absorpcyjnej występowania na ścieżce pomiarowej zmiennego stężenia badanego związku. Problem ten jest szczególnie istotny w przypadku wykonywania pomiarów dla długich ścieżek optycznych. Pomiary tego typu są wykonywane m.in. przy kontroli składu środowiska w kotłach energetycznych przy współspalaniu biomasy i węgla. (Wpływ niejednorodności stężenia gazu na dokładność pomiarów w spektroskopii absorpcyjne).

Keywords: absorption spectroscopy, gas concentration.
Słowa kluczowe: spektroskopia absorpcyjna, koncentracja gazów.

Introduction

Absorption spectroscopy is a measurement method that is widely used, among others in combustion process diagnosis [1, 2]. Its main advantage is lack of interaction with a environment to be controlled as well as high rate of obtaining measurement results. It is very important, especially in the case of controlling rapid processes such as combustion.

Coal combustion is still one of the commonest ways of electrical power production. More and more rigorous regulations concerning acceptable levels of combustion gases emissions as well as the required percentage of renewable energy have leaded to spread coal-biomass co-combustion technologies in existing power plants with different types of biomass.

Operating a combustion process is complicated for large number of factors affecting its course such as: the temperature inside a combustion chamber and its distribution, air-fuel ratio, fuel composition. For the mentioned above reasons, combustion of pulverized coal is relatively a complex process to run, especially when additions of biological origin are mixed with pulverized coal. Apart from problems connected with appropriate preparing of fuel mixture, e.g. difficulties with size reduction of wood waste, flame stability issues can occur and flame-out is possible.

A very important consequence of biomass-coal co-combustion in power boilers are changes in atmosphere composition. Research have shown [3] that atmosphere composition inside a power boiler greatly influences intensity of corrosion processes.

The proper operating of a combustion process requires an access to many various measurement signals, including signals of gas composition.

Problems arise when spectroscopic methods for gas composition measurement inside power boilers are applied. Usually, it is assumed that laser beam runs through measurement path of homogeneous environment. Such an assumption means that there is constant value of gas mixture concentration, constant pressure as well as temperature. It is suitable only in laboratory measurements, where samples are properly prepared and measurement path is short. Examining composition of a gas mixture inside a power boiler requires relatively long measurement path, that could be located e.g. across combustion chamber. The mentioned above parameters are not constant in the case being discussed. Therefore, it is necessary to take into account influence of measurement path inhomogeneity on measurement accuracy.

Principles of absorption spectroscopy

A light beam passing through a transparent medium undergoes reflection, scattering and absorption phenomena. For years, absorption is utilized for both quantitative and qualititative chemical analysis of the examined medium. It results for absorption coefficient is dependent on content of the measured substance within the medium. The Beer-Lambert law relates the absorption of light to the properties of the medium through which the light is travelling as:

$$(1) \qquad \frac{P}{P_0} = e^{-\sum_i S_i g(v) p x_i L}$$

where P_0, P – intensity of incident and passing radiation respectively , S_i – spectral line intensity for the i-th factor (cm^{-2}atm^{-1}), $g(v)$ – spectral line profile function, p – total pressure (atm), x_i – mole fraction of the i-th fraction, L – measurement path length(cm).

Both spectral line intensity and its profile function depends on measurement condition, especially temperature and pressure [6]. Thus, inhomogeneity of the medium to be measured along measurement path affects the results obtained.

The atmosphere inside the power boiler

Gas mixture composition inside a power boiler is diversified considerably and depends mainly on chemical constitution of a fuel. Biomass co-combustion with coal leads to formation many gaseous products, that cannot be observed when only pulverized coal is burned.

Moreover, for the large size of a power boiler and the way combustion process is organized, atmospheric composition is different for given point of a combustion chamber as well as a flame. A proper utilization of fuel requires formation of a proper areas that differs in oxygen content Thus, contents of the other components is also different within a combustion chamber.

As it was pointed out in [3, 4], changes in composition of a mixture is relatively high. It results in distinguishing a special area within a combustion chamber called near-wall zone.

The main components of the combustion chamber atmosphere are: nitrogen, carbon monoxide and dioxide, water vapor, oxygen and both nitric and sulfur oxides. Their fraction in combustion chamber atmosphere depends on

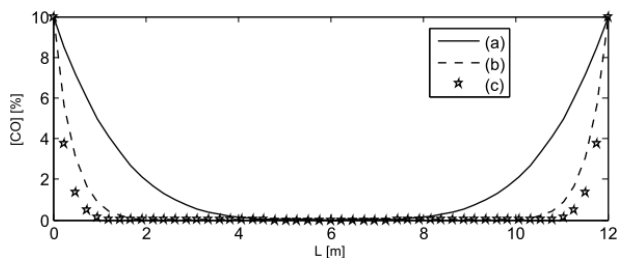many factors. An example profile of CO concentration distribution in power boiler is shown in figure 1.

Fig.1. An example CO concentration distribution inside a power boiler

Simulation studies - assumptions

Due to presence of concentration inhomogeneity of atmospheric components inside a combustion chamber of a power boiler a question arises how it affect results of spectroscopic measurements. Thus, simulation research have been done in case of variable CO concentration distribution inside a combustion chamber.

The following assumptions have been made adopted: the measurement path was 12 m length, total pressure (that equals 1 atm) was constant along the path and the temperature was 1073K. For the sake of calculation simplicity, measurement path was divided into 600 segments, where the gas concentration is homogeneous. CO concentration profile was accepted as the approximation functions that are presented in figure 1, profile marked as (a) - polynomial of 4th order (dashed line), (b) – polynomial of 14th order (solid line), (c) – polynomial of 24th order (star). The second profile corresponds to more homogeneous conditions as opposite to (a) profile, third – to more than a second.

Inhomogeneity degree of the profiles can be assessed by comparison of standard deviation, variance and maximum of absolute deviation. The profiles are described by the parameters depicted in table 1.

Table 1. Parameters of the analyzed CO concentration profiles

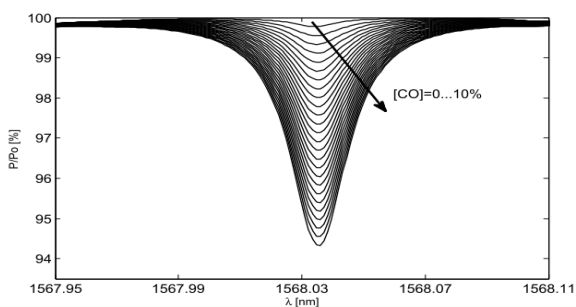| profile	(a)	(b)	(c)
standard deviation	0.4038	0.1993	0.1608
variance	0.1631	0.0397	0.0258
maximum of absolute deviation	8	9.4	9.8

Fig.2. Changes of shape CO line corresponding to concentration rise from 0 % to 10%

It was assumed, that atmospheric composition is typical for combustion chamber of a power boiler. Its main components are carbon mono- and dioxide as well as water vapor with 10% of $[CO_2]$ and $[H_2O]$ while amount of CO varies according to the assumed profile - from 0% to 10%. The analysis has been done within the spectral range from $1.558\mu m$ to $1.570\mu m$. Within the discussed spectral range, taking into consideration typical gas mixture that is present

inside a combustion chamber, only CO, CO_2 and H_2O have enough strong absorption lines that makes quantitative analysis possible. The other gas mixture components have no an effect on a shape of absorption spectrum being analyzed for they have no or very weak absorption lines, that could be neglected [5]. In the presented simulation, in order to determine absorption spectrum of gas mixture, the HITRAN database has been used [6]. Change in shape of the considered CO absorption line (λ=1568,035nm) due to change of concentration is presented in fig. 2

Results

Absorption spectra that were obtained for measurement paths with profile (a) and (b) were shown in fig. 3a and 3b respectively as well as spectra for average ([CO]avg.) and minimum ([CO]avg.) CO concentration along the path. Absorption spectrum obtained for maximum concentration ([CO]max.) can be seen partially, for the fact that absorption values are much higher for the next cases and it would make the spectral plot illegible. Below, for the spectra being discussed dependences of spectral misfit for average and resultant spectra.
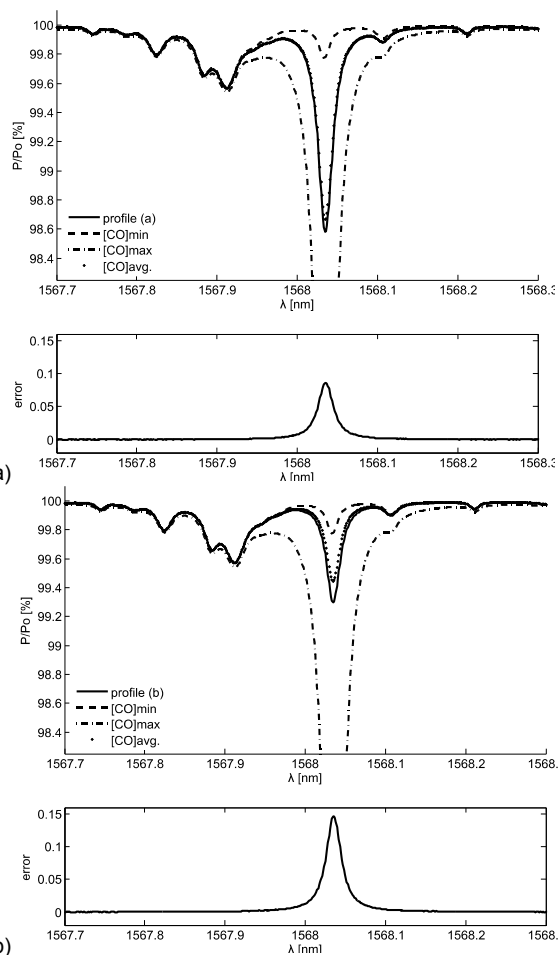

Fig.3. Absorption spectra for measurement paths (concentration: minimal [CO]min, average [CO]avg., maximum [CO]max)

It could be observed in fig. 3, that CO absorption line are surrounded by absorption peaks of the other gases. The proper selection of the wavelength range makes the analysis immune to neighboring absorption lines.

A comparatively strong similarity among the absorption lines for the whole measurement path and mean concentration is presented in fig. 3. The line misfit is as high as 0.09%. It is not a high value, especially when compared

with the (b) profile. In the second case, the misfit error is as high as 0.15% and for the (c) profile reaches 0.12%.

The results of the carried out analyses is shown in fig. 4. The figure presents comparison of spectra shape, that were obtained for the three concentration profiles with spectra corresponded to the maximum and the mean concentration values.

Comparing the presented spectra one can notice their different shape. Measurement results will depend, among other things, on the spectroscopic method that is applied. If a direct method is utilized, where an absorption peak is analyzed, measuring error depends on concentration profile as it is depicted in table 2. Results for the method based on an area under the curve are also shown in table 2.
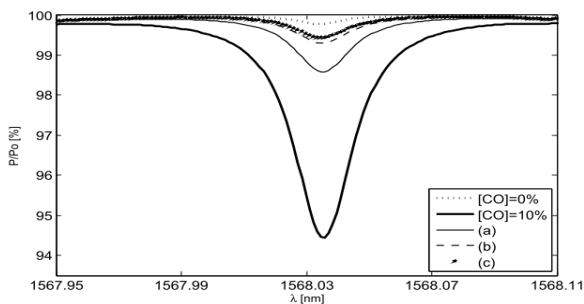

Fig.4. Transmission spectrum of a gas mixture for different profiles of CO concentration changes in the measurement path

Table 2. Dependence of CO concentration error in a gas mixture due to inhomogeneous concentration along the measurement path

profile type	(a)	(b)	(c)
$[CO]_{avg.}$	2%	0,6%	0,2%
measured absorbance	0,1293	0,0625	0,0499
absorbance at $[CO]_{avg.}$	0,1212	0,0489	0,0386
error relative	6,68%	27,81%	29,27%
absorbance at $[CO]_{max}$	0,534	0,534	0,534
error relative	-75,79%	-88,30%	-90,66%
measured absorption peak	98,5814%	99,2981%	99,4333%
absorption peak at $[CO]_{avg.}$	98,6674%	99,444%	99,5555%
error relative	-0,09%	-0,15%	-0,12%
absorption peak at $[CO]_{max}$	94,3354	94,3354	94,3354
error relative	4,50%	5,26%	5,40%

It could be observed that the "measured" absorbance for all profiles is higher than the absorbance obtained for the concentration of the mean profile. Assuming that such a measurement should provide information of a mean CO concentration along the measurement path, the result is overestimated for CO concentration unhomogeneneity. The measurement error reaches its maximum for the (c) profile. It could be explained by the fact that gas layers located close to the boiler wall attenuate the signal enough strong that it has the greatest influence on measurement results in spite CO centre of gravity are practically transparent.

Comparison of simulation results for the maximum CO concentration along measurement path allows to assess the usability of the mentioned methods for estimation of CO concentration near boiler's walls. As it follows from results collected in table 2, estimation error of absorption for the all profiles excesses 75%. It disqualifies the method. For the

determination of the peak absorption errors oscillate around 5%, that could be assessed as a rewarding result.

The smallest errors were obtained between the "measured" absorption peak and the absorption peak that was obtained for mean concentration along the path. They are not higher than 0.15%.

Conclusions

The presented analysis shows influence of concentration changes of a given component on absorption spectrum of a gas mixture that is typical for combustion chamber of power boiler. Change in spectrum shape in the discussed conditions causes errors in determination of gas mixture contents.

The carried out simulations have shown, that in order to maintain measurement correctness it is necessary to take into account concentration profile of a given component along the measurement path.

It was shown, that degree of inhomogeneity (measured by e.g. standard deviation, variance and/or maximum of absolute variation) has a considerable influence on measurement errors, if absorbance is analyzed. In this case errors are considerable if a given medium is slightly unhomogeneous and has high values of maximum absolute deviation. Absorption peaks analysis results in lower errors comparing to the absorption analysis errors, but it sensitive to measurement noise.

It should be remembered that in real conditions inhomogeneity is not only narrowed to concentration, but also temperature inhomogeneity should be taken into consideration. It makes the whole analysis even more complicated. Acquaintance of concentration profile as well as application of advanced analysis methods should ensure concentration determination of a given substrates, keeping a minimal error even in case of considerable medium inhomogeneity inside a power boiler.

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