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Optoelectronic CO Concentration Analyser – Wavelength Selection

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One of the most important requirements that have to be met by the contemporary power industry is limitation of emission of substances polluting the natural environment to the values specified by standards. Nitrogen oxides (NOx) are considered to be one of the most dangerous. In order to reduce them the so-called low emission technologies are used. They consist in graduation of air and fuel amount in a burner itself as well as within a combustion chamber. It results in creation of reach and lean zones. Air deficiency causes NOx reduction and inhibits NOx creation. Surplus air in the next zone of allows combustion of remains of unburned fuel.

The price of such technique of limitation of NOx emission is increase of unburned particles coefficient and increased corrosion of boiler's elements (the high-temperature or low-oxygen corrosion). The increased level of unburned particles results in overall efficiency deterioration. Increased corrosion may lead to necessity of more frequent repairs what means increased costs of operation.

It is assumed that the intensity of the low-oxygen corrosion rapidly rises when oxygen concentration in the near wall layer drops below 1%. Corrosion velocity strongly depends on carbon monoxide concentration and varies from 8nm/h at CO concentration around thousands ppm, to even 300mm/h at CO concentration exceeding 3%. In Polish power boilers CO concentrations of even 8% and the corrosion velocity of 600nm/h were observed [4, 5].

It impossible to avoid the low-oxygen corrosion, nevertheless it can be limited by appropriate control of the combustion process. It is possible to create conditions for both NOx reduction and corrosion minimisation by such control of the process that does not allow excessive CO concentration and O_2 concentration drop in near wall layer of the power boiler. Continuous measurement of concentration of these gases is therefore necessary. Measurement environment is characterised by the high temperature (about 750K) and dustiness.

Absorption spectroscopy allows a continuous measurement of concentration of gases in the near wall layer. It is based on decay of intensity of light passing through the mixture of gases. It is described by Lambert – Beer law:

$$I_1(\nu) = I_0(\nu) \cdot e^{-\alpha(\nu)\cdot P \cdot L},$$

where $\nu = 1/\lambda$ denotes wave number, $I_0(\nu)$ is an initial intensity of light and $I_1(\nu)$ is an intensity of light after passing path-length L through a gas at pressure P and absorption coefficient $a(\nu)$.

A spectral absorption coefficient is a parameter characteristic for a given gas and can be determined from the following formula:

$$a(\nu) = \frac{7{,}34 \cdot 10^{21}\left[\dfrac{mol \cdot K}{cm^3 atm}\right] S[cm/mol] \cdot g[cm]}{T[K]},$$

where T is the temperature, g is the function describing a shape of absorption line (considering, among others, line self-broadening, Doppler broadening etc.) and S is the line strength (which can be obtained from e.g. HITRAN database).

There are many measurement techniques employing the absorption spectroscopy that differ in accuracy, response time, concentration range and so on. Figure 1 shows schematic diagram of the proposed measurement device employing non-dispersive correlation spectroscopy. Two sources of light, correlation cell, neutral cell and detector are the main components of the device. The light from source 1 is passing through the correlation cell. The cell contains carbon monoxide of known concentration such to obtain clear absorption lines of desired component in output spectrum. The light is subsequently passing through the medium under investigation and then is detected. Alternately (with source 1) the source 2 is switches on and its light is passing through the neutral cell and then at the same path-length is passing through the medium under investigation and is detected by the same detector. The light leaving neutral cell does not contain absorption lines of measured component, they appear after passing through the medium under investigation.

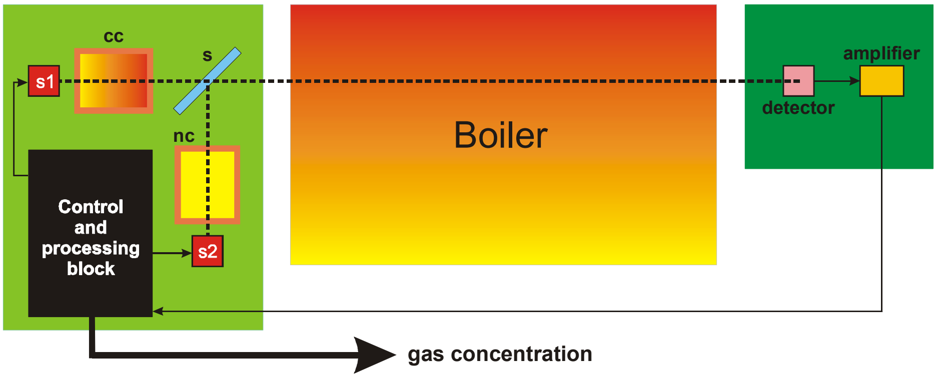


Fig. 1. Schematic diagram of analyser for CO concentration measurement in near wall layer of power boilers. (s1, s2 – light sources, cc – correlation cell, nc – neutral cell, s – optical coupler

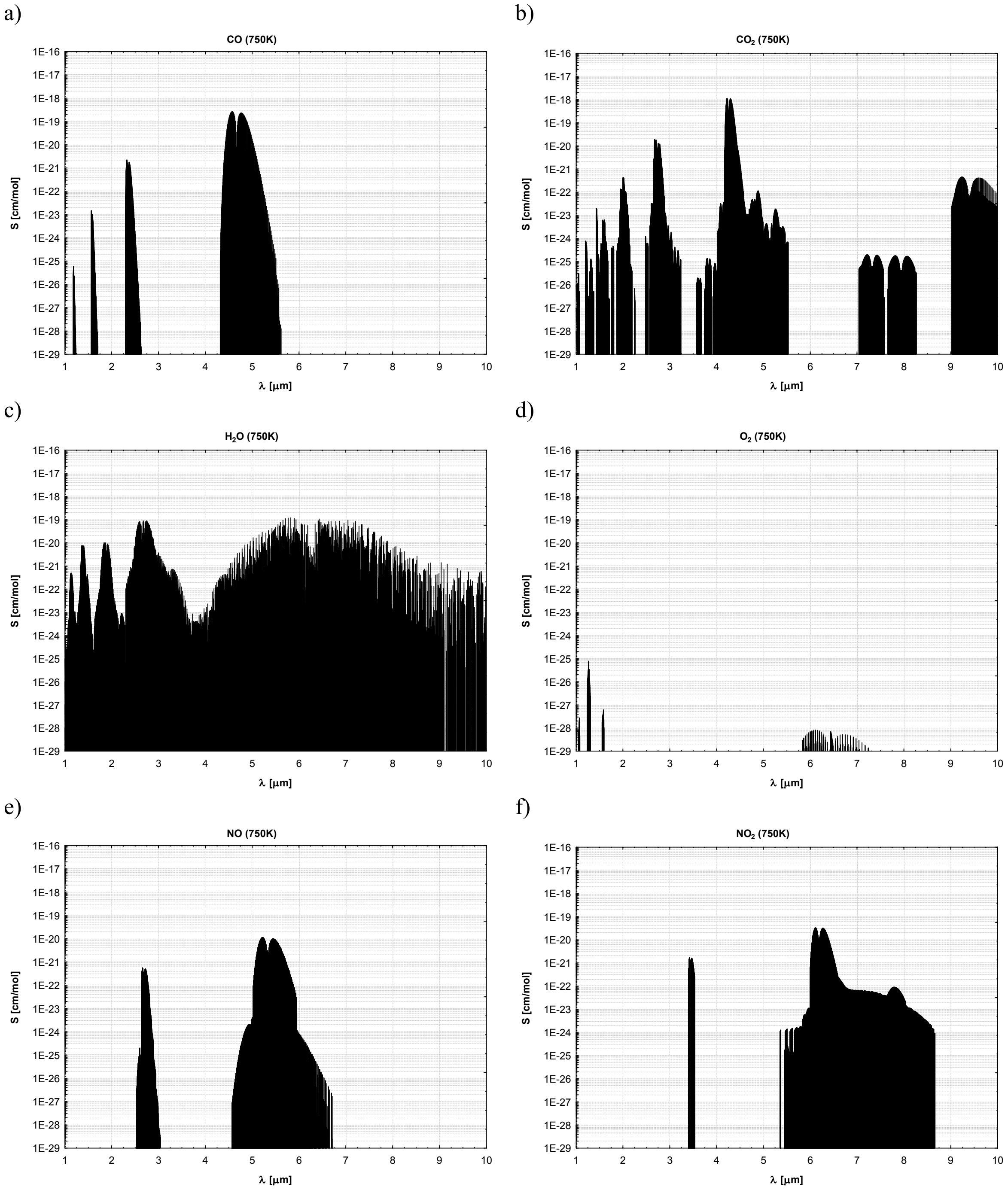


Fig. 2. Absorption spectra a) CO, b) CO_2, c) H_2O, d) O_2, e) NO, f) NO_2 for 1 ÷ 10 μm band

Correlation between spectral lines originated by both sources of light allows very selective determination of concentration of the gas.

Attenuation of the light bundle at given wavelength is determined by all gasses absorbing at this spectral line. The atmosphere inside boiler is composed by many gases – H_2O, CO, CO_2, NO, NO_2, O_2 have the most important share. Figure 2 shows their absorption spectra within 1 and 10 μm at 750K.Carbon monoxide (fig. 2a) the strongest absorption exhibits at 4,3 to 5,6 μm, a little weaker at 2,3 – 2,6 μm (I overtone), 1,55 – 1,65 μm (II overtone) and around 1,2 μm (III overtone).

Absorption line intensity is directly associated with path-length choice, The higher is the spectral line intensity the shorter path can be used, even for small concentrations. Optimal spectral line for carbon monoxide measurements would be chosen from 4,3 to 5,6 μm band, because main absorption lines are situated there.

The most difficult problem seems to be proper spectral line selection from the point of view of spectra overlapping between measured gas and the other components of the mixture. Main absorption lines of CO overlap with those of NO, NO_2, CO_2 i H_2O. Absorption spectrum of water overlaps carbon monoxide lines in 2,3 – 2,6 μm band as well as for the third overtone. The second overtone band appears to be the best choice because it is relatively weakly overlapped by other gases' spectral lines.

Availability and usability of light sources and detectors is another criterion of wavelength selection. Semiconductor sources seem to be the best choice because of their small dimensions, narrow spectral lines, tunability, etc. The 3 to 30 μm band is sometimes called "the fingerprint" since non overlapping spectral lines of many gases are situated there. There are commercially available LEDs and lasers for this band (fig. 3) [2], however, they are characterised by relatively short operation time (several hundreds of hours) and the necessity of intensive cooling (200K) [2,3]. It increases cost of analyser and complicates its construction. As far as the considered criterion is concerned LEDs and semiconductor lasers emitting in the band 1 to 2,5 μm appear to be better by reason of their long operation time and operation temperature close to the room temperature. Technology of production sources for the so-called transmission windows (around 850 nm, 1310 nm and 1550 nm) is well developed. It allows production of cheap lasers of power of tenths of mW, easily tunable, fast, operating at room temperature with MTBF of several years [1,2]. Therefore they are the best candidates to be used in the cheap optoelectronic gas analyser.

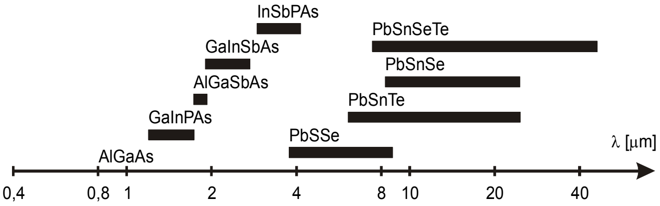
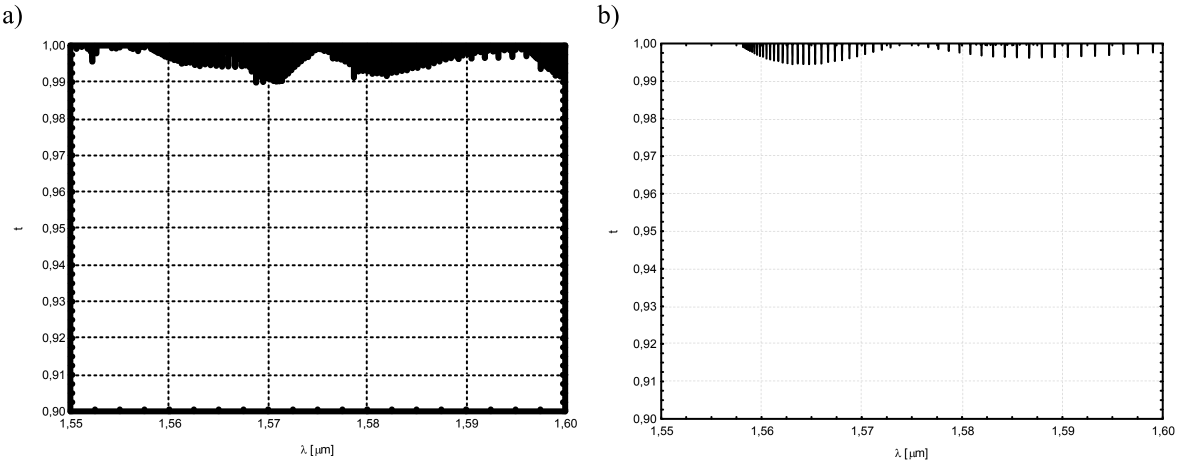


Fig. 3. Operation spectral bands of semiconductor sources of light

In the light of the above considerations the utilisation of light sources emitting within 1,55μm and 1,6μm appears to be justified. Figure 4 depicts transmission spectra of a mixture of gasses for this band. The spectra were obtained using the HITRAN 2000 database for the temperature 750K and for two optical path lengths: 1m (fig.4a) and 10m (fig.4c). The mixture consisted of H_2O – 10%, CO – 4%, NO_x – 600ppm, CO_2 – 17%, O_2 – 20% and complementary N^2, which does not absorb within the considered spectral band. The composition of the mixture respond to the obtained in measurements made in the Institute of Power Industry in Warsaw using traditional methods.

An attenuation of a laser beam is not too high for the considered cases, nevertheless it seems to be sufficient for measurements. Comparison of the two diagrams confirms the fact that longer path length means better accuracy. Unfortunately, inside a boiler it is usually technically impossible to obtain such long optical path length without multiple reflections. A proper choice of optical path length is then a separate and quite important problem. Detection of carbon monoxide within a wide range of its concentration requires determination of an optimal path length or its variation in dependence on CO concentration.

Comparing plots (a) and (b) as well as (c) and (d) one can notice that in the considered spectral band groups of CO absorption lines that do not overlap with lines of other gases can be chosen. A vicinity of 1.565μm is such region.



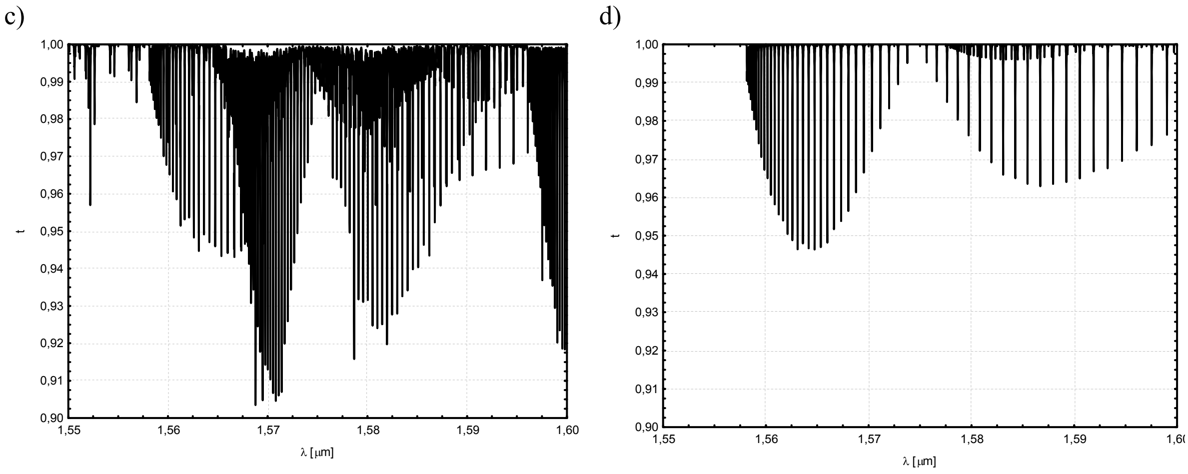


Fig. 4. Transmission spectrum for the chosen mixture of gasses at 750K at different optical path lengths: 1m (a) and 10m (b) as well as for carbon monoxide isolated-out at the same conditions: (b) and (d) respectively

The brief review of phenomena proceeding in low-emission combustion as well as review of problems of measurements of CO concentration in mixture of gases allow to draw the following conclusions:

- continuous measurement of CO concentration in the near wall layer of industrial boilers allows detection of corrosion intensity growth so it allows counteraction;
- near infrared absorption spectra overlapping of flue gasses requires application of special techniques for determination of concentration of chosen components;
- strong absorption lines within 4,3 – 5,6 μm band would allow measurement of low concentration of carbon monoxide at relatively short optical path length;
- the best choice for CO concentration measurement seems to be 1,55 – 1,60 μm band because of availability, good operation parameters and low price of semiconductor sources and detectors as well of weak spectra overlapping of mixture components and relatively strong CO absorption lines.
- The length of an optical path is strongly affecting accuracy. Its choice has to be made considering expected CO concentrations as well as technical feasibility of measurements.

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Aprašoma 4,3–5,6 μm juostos ilgio įtaka sugėrimo procesui, kai matuojama esant žemo lygio karbido monooksido koncentracijai. Nurodoma, kad atliekant matavimus esant tokiai CO koncentracijai, geriausias atvejis yra 1,55 – 1,60 μm ilgio juosta. Taip užtikrinamas geriausias parametrų valdymas, mažiausia puslaidininkinių šaltinių ir detektorių kaina. Teigiama, kad optinio tako ilgis lemia eksperimento tikslumą. Il. 4, bibl. 5 (anglų kalba; santraukos lietuvių, anglų ir rusų k.).

W. Wójcik, P. Komada, S. Cięszczyk, I. Manak, T. Golec. Optoelectronic CO Concentration Analyser – Wavelength Selection // Electronics and Electrical Engineering. – Kaunas: Technologija, 2004. –No. 1(50). – P. 5–8.

Strong absorption lines within 4,3 –5,6 μm band would allow measurement of low concentration of carbon monoxide at relatively short optical path length. The best choice for CO concentration measurement seems to be 1,55 – 1,60 μm band because of availability, good operation parameters and low price of semiconductor sources and detectors as well of weak spectra overlapping of mixture components and relatively strong CO absorption lines. Ill. 4, bibl. 5 (in English; summaries in Lithuanian, English, Russian).

В. Войцик, П. Комада, С. Ченжщык, И. Манак, Т. Голец. Оптоэлектронный анализатор СО концентрации волновой длины // Электроника и электротехника. – Каунас: Технология, 2004. –№ 1(50). – С.5-8.

Описывается влияние длины на процесс абсорбции в диапазоне 4,3-5,6 мкм. Доказано, что наилучшим случаем является диапазон 4,3–5,6 мкм. В данном случае получается максимальная точность и минимальная цена полупроводниковых источников и детекторов. Указывается, что СО концентрация во время продолжительных измерений позволяет установить условную длину линии абсорбции.Ил. 4, библ. 5 (на английском языке; рефераты на литовском, английском и русском языках).