LED-based NDIR natural gas analyzer

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Abstract. A new generation of the light-emitting diodes (LEDs) and photodiodes (PDs) was used recently to develop an open path non-dispersive infrared (NDIR) methane analyzer. The first open path detector prototype was constructed using LEDs for measurement and reference channels, accordingly, and first measurements for methane gas have been performed using optical paths of the order of several meters [3]. The natural gas consists of several first alkanes, mainly methane, and it is important to have a possibility of measuring all of them. In the present work we report the results of NDIR measurements for propane-butane mixture and new measurements of methane using LEDs for measurement and reference channels at 2300 and 1700 nm wavelengths, accordingly. The necessity of the double beam scheme is demonstrated and obtained results for methane and propane-butane mixture are compared.

1. Introduction

Low cost and low power consuming methane detection is needed for control of large areas both for pipeline inspection and for pollution control. Mainly point sensors have been developed for natural gas detection – catalytic, semiconductor and optical ones [1-3]. However this kind of sensors provides the measurements only in the place were they are mounted. To enable the large area monitoring these sensors should be joined in a sensor network (or wireless sensor network [4]). The number of sensors in a wireless network for combustive gas monitoring should be tens or even hundreds, but still a chance exists that the natural gas leakage won’t be detected. Therefore optical open path detection systems have been developed using different light sources – mainly xenon lamps, LEDs and lasers in order to provide long distance measurements. Gas sensors based on optical absorption offer fast responses (time constants below 1 s), minimal drift and high gas specificity, with zero cross response to other gases [3]. Xenon lamps and LEDs are used for non-dispersive measurements with rather broad light spectra with the width of the order of hundreds of nm, while laser diodes and lasers - for tunable spectroscopy with very narrow spectra with the width of tenth of a nm. But laser systems are rather expensive, while xenon lamps systems are rather high power consuming ones and besides need protecting shields, enlarging essentially the size of the constructions. So the best candidates for low cost and low power consuming systems are LED-based systems. Recently qualitative technological break-through in growing of narrow band-gap heterostructures was achieved [5]. High effective LEDs for the spectral range 1600-5000 nm and spectral matched photodiodes were developed. For developing of LEDs and PDs lattice-matched heterostructures with GaInAsSb quaternary solid solutions in the active layer were used. It became possible to create gas sensors that meet all demands of the mass market: compactness; low electrical power consumption; high selectivity; high sensitivity; long life-time without additional calibration and low cost in mass production. Average optical power up to 3.5 mW and peak power up to 170 mW was achieved for 1600-2400 nm LEDs. Typical LED spectral widths are comparable with the width of methane absorption bands. It was shown recently that for methane concentrations of the order of Low Explosive Limit (LEL) the highest sensitivity could be achieved by using absorption band at 2300 nm wavelength (for high values of the product of concentration by optical path the light transmission for the strongest absorption bans goes to zero) [6].

NDIR transmission is described by integral formulation of Beer-Lambert low:
where \( \nu \) is the frequency, \( K(\nu) \) is the frequency dependent linear absorption coefficient, \( I_0(\nu) \) is the light source spectra and \( F(\nu) \) is the sensitivity of the photodetector, \( L \) – the optical path in the absorbing media. Coefficients \( K(\nu) \) are usually obtained from HITRAN database [7]. For large values of the argument in the exponent the transmission for the strongest absorption band becomes too low and it is more efficient to work with a weaker absorption band. It’s important only for open path detectors measuring concentrations near LEL level, for trace gas detectors, measuring concentrations on ppm or lower level, the most efficient for measurements is the strongest absorption band.

One of the peculiarities of NDIR detection scheme is the use of two channels – a measurement and a reference one. Emission wavelength of the reference beam should be shifted from the measurement one, so that the reference signal won’t be absorbed by the specified gas. The total measured intensity is normalized to the intensity of the reference channel in order to exclude the scattering and absorption effects that may occur along the whole optical path due to atmospheric precipitations or other obstacles.

The NDIR gas analyzer was invented and first used in Germany in the 1930’s. Recent breakthrough in LEDs technology permitted one to use nonconventional IR light sources for gas detectors. Firstly LEDs/PDs pairs were used in portable trace gas analyzers [8] and a bit later - in open path ones, the construction of an open path IR hydrocarbon gas detector, based on heterostructure PDs and LEDs, being reported in [9]. The 3400 nm measurement wavelength was used for methane main absorption band detection, the reference wavelength being available in two options – 3070 and 3850 nm and the optical path being of the order of 40 m. Now LED-based NDIR detectors are mainly used as trace gas analyzers [3,10]. Considering distances much more than 40 m, we are developing natural gas NDIR detector using absorption band at 2300 nm. The only problem in this case is in choosing the appropriate LED for the reference channel with a spectrum close to the spectrum of the measurement LED and outside the methane and water absorption bands at 2300 and 1900 nm, accordingly. Also one should take into account that for existing LEDs there is a gap in wavelength from about 2.4 to 2.8 \( \mu \)m due to existence of miscibility region for GaInAsSb based solid solutions which depends on the epitaxy temperature and the compound composition. Considering the currently available LEDs the only possibility to solve the problem with reference beam is to use the LED with 1700 nm peak, nevertheless it crosses the methane absorption band at 1650 nm (Figure 1). This cross-reference can be excluded by renormalization of calibration curve due to the fact that this band is much weaker than that at 2300 nm. The first preliminary results of methane concentration measurements by LED-based NDIR prototype analyzer in measurement channel were reported recently [6]. Now the measurements in the reference channel are also possible.

![Figure 1. LED spectra and methane and water absorption bands](image-url)
The natural gas consists of several first alkanes, mainly – methane, absorption bands being rather similar for all of them. LELs of the main components of the natural gas are given in Table 1. For most combustible gas sensors the default alarm is set as 10 % of LEL with a full range 0 – 100 % LEL.

| Component | LEL (vol. %) |
|-----------|-------------|
| Methane   | 4.4         |
| Ethane    | 2.5         |
| Propane   | 1.7         |
| i-Butane  | 1.4         |
| n-Butane  | 1.3         |
| Pentane   | 1.4         |

Structurally, the alkanes are quite simple, having no functional groups. They form a homologous series differing only in the number of methylene (–CH₂–) segments. The first and lowest-weight alkane in the series is methane, CH₄, which is quite atypical of the series because the carbon atom is tetrahedrally coordinated to the four hydrogen atoms, and it contains no C-C bonds [11]. Alkanes IR spectra display only C-C and C-H bond vibrations, being somewhat self-similar: the same absorption bands are present in essentially the same positions, differing only in such less obvious yet still diagnostic characteristics as absorption depth and band width. As a result the cross sensitivity is present for practically all low number alkanes. Nevertheless the sensitivity of NDIR method depends on the particular alkane, and we have performed NDIR measurements of propane-butane mixture in order to compare the results with data for methane. One of the ways of improving NDIR selectivity is the use of additional selective reflector [12], it could be rather easily incorporated in an open path gas analyzer if needed, but in the current paper we are considering only the simplest NDIR scheme, in which the absorption coefficient integrated over the whole emitting band width is measured.

2. Experimental
Prototype NDIR analyzer consists of two independent units – emitting and detecting blocks mounted on tripods (Figure 2 a, b). It’s construction permits one to use at a time only one channel (measurement channel at 2.3 µm or reference one at 1.7 µm), so that full NDIR measurements should be performed successively. In optical scheme one collimating lens is used in the emitting block and one focusing one in the detecting block.

![Figure 2. Photo of the prototype NDIR analyzer blocks (a – emitter, b – receiver)](image-url)
In emitting and receiving blocks “LED Microsensor NT” LEDs and PDs are used [13]. These LEDs are characterized by compact size of 0.35-0.35 mm, low power consumption (<1 mW), short response time – 10-50 ns, operation temperatures up to +150°C, lifetime 80 000 hours. LEDs are mounted into a package with a thermoelectric module (Peltier element) enabling LED chip temperature stabilization. Besides there is a possibility to arrange multi-element arrays enabling to obtain multi-wavelength emitters in single compact packages. The PD characteristics are following: cut off at wavelength 2.45 μm (Figure 3), sensitive area diameter 0.3 mm, detectivity 2.5×10¹⁰ cm Hz⁻¹⁄₂ W⁻¹ [10].

![Figure 3. PD spectral response [13]](image)

Propane-butane mixture (30% propane + 70% butane) was chosen for NDIR analyzer testing. Firstly the measuring channel at 2.3 μm was checked, the gas cell of the length of 10 cm was filled with propane-butane mixture) and then - with air. In Figure 4 it is shown that the NDIR intensity is lowered when the gas cell is filled with testing gas and is restored very well after it is filled once more with air, the noise being on the level of several tenths of a per cent.

![Figure 4. Transmission in propane-butane mixture (optical path 10 cm)](image)

Secondly, the reference channel at 1.7 μm was checked, and it was shown, that the variation of the reference signal due to absorption is much less than of the measurement one, so that the signals ratio could be used in NDIR double beam scheme as calibration curve (Figure 5, curve 23/17).
Thirdly, the necessity of a double beam scheme was demonstrated for methane measurements. The gas cell was filled with 100% methane and successive measurements were performed both for measurement and reference channels. The results are depicted in Figure 6 together with the theoretical lines calculated using HITRAN database [7]. It is seen that both experimental curves are lower than theoretical ones the difference being practically the same. This difference is about 15 % for reference channel and is associated with some additional scattering or absorption in the gas cell. It’s much stronger than the noise and its influence can be excluded only by normalizing the measurement channel intensity to reference channel one. The comparison of renormalized NDIR transmittances shows, that in methane the absorption effect is by 70% stronger than in propane-butane mixture.

Figure 5. Transmission in propane-butane mixture (23 – measurement channel, 17 – reference one, 23/17 - calibration curve)

Figure 6. Transmission in 100% methane (23 – measurement channel, 17 – reference one, hitran 23 and HITRAN 17 – corresponding HITRAN-calculated curves)
One should note that methane LEL is equal to 4.4% (table 1). The usual unit in open path measurements is LEL/m (the integrated over all optical path concentration divided by LEL value and one meter). The open path gas analyzer should measure concentrations in the range 0 – 100 % LEL/m. The dangerous level for methane concentration in air is considered to be 50% of LEL/m or 2.2% m.

For half a meter optical path the corresponding LEL/m value is 25% which results in absorption on the level of 3.3%, being much higher than the sensitivity threshold of the constructed analyzer prototype (the noise is on the level of a tenth of a per cent). It means that the constructed gas analyzer could be used as a reliable alarm device for dangerous methane concentrations detection in the range from several to hundred % LEL/m.

3. Conclusions

It is shown that LED-based NDIR detectors with a 2-channel optical scheme are very perspective for alkane open path analysers of gas concentrations near LEL. For the first time LED with a peak emission at 2.3 μm is used in the measuring channel and 1.7 μm LED – in the reference one. It is shown that the influence of alkane absorption band near to the reference emitter spectrum can be excluded by renormalization of the calibration curve. The first prototype of an open path LED-based detector was constructed and the first measurements have shown that the methane concentration could be measured with a bit better sensitivity than for other alkanes.

From figure 6 it is seen that in the double beam scheme for optical path 10 cm the pure absorption in 100% methane is rather low (of the order or 15%), while the absorption band at 2.3 μm is rather strong by itself. It results from the fact, that LED linewidth is wider than the absorption band width and that absorption spectrum is discrete while the emitting spectrum is continuous one (figure 1). As a result essential part of light is not absorbed at all propagating through methane. To enhance the absorption effect the filters, narrowing LEDs spectra, could be used or a selective reflector before the photodiode could be added [11]. Such modifications should improve the sensitivity of an open path analyzer enhancing the signal to the background ratio.

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