“Instruments for Methane Gas Detection”

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ABSTRACT
This paper gives the explanation of different instruments for detecting methane gas in detail. This paper discusses their working principles. Methane gas detection is essentially required in the areas like in coal mines, power plant, Waste Water Treatment, Boiler Rooms etc. This paper also discusses their roles in various applications.

KEYWORDS: Tunable Diode Laser Absorption Spectroscopy (TDLAS), synthetic natural gas (SNG), wavelength modulation spectroscopy (WMS), LMLD (LED Methane Leak Detector), Flame Ionization Detector (FID), Gas chromatography (GC), volatile organic compounds (VOCs).

I. INTRODUCTION
Methane gas detection is very important because this gas is not only an explosive but also acts as asphyxiant. It can therefore cause serious harm to you and your family's health and home. Methane gas detection was pioneered in the twentieth century by coal miners who used canary birds that would pass out if there were any spike in the amount of methane in the atmosphere. Thankfully, methods of methane gas detection have moved on from this primitive means of highlighting its presence in the air. There are now a number of methods and devices you can use for methane gas detection. Before discussing these methods of methane gas detection, let us look at why the gas poses such a threat to human health. Methane can lead to explosions in coal shafts - the gas trapped in the rock can be released as a result of mining - and also fires in landfill sites as a result of a process known as methanogenesis. In the home, methane is found in the natural gas used for cooking. There is also a risk of methane leaking into your home from sewer pipes.

Methane in the atmosphere is dangerous because our lungs only function normally when the atmospheric concentration of oxygen is more than twenty per cent. If the level falls below this, including as a result of it being replaced by methane, it can trigger asphyxiation and if undetected will ultimately lead to death. Let us now turn to the various methods of methane gas detection. As methane is odorless and colorless, it can be very difficult to detect. A methane gas detector is by far the best method of alerting yourself to the presence of this gas in the air around you. Methane gas detectors are normally portable so that you can carry them around in your kitchen or near sewers to pick up the presence of methane gas. If you use a fixed methane gas detector it should be installed high up near the ceiling because methane being lighter than oxygen rises to the top of whatever space it is in.

Methane (CH4) is the principal component (97%) of natural gas. Methane is a colorless, odorless gas, which is lighter than air. It is formed by the decomposition of organic carbons under anaerobic conditions. Methane is abundant in nature and thus a desirable fuel. However, since it is a gas at normal temperature and pressure, it is difficult to transport from its source. It is generally transported in bulk by pipeline or liquefied natural gas (LNG) carriers. Natural gas is found with other fossil fuels, in coal beds, as methane clathrates, and is created by methanogenic organisms in marshes, bogs, and landfills. It is an important fuel source, a major feedstock for fertilizers, and unfortunately a potent greenhouse gas. Methane gas is flammable and therefore should be monitored in enclosed or underground spaces such as mines or power plant. It also poses the danger of asphyxiation, as it displaces oxygen. Also carbon monoxide is a byproduct of methane, so proper ventilation is critical.

II. INDUSTRIAL APPLICATIONS OF METHANE GAS DETECTORS
Some of the industrial applications of methane gas detectors are as follows:

1. POWER GENERATION
Natural gas is often used to generate electricity by means of gas turbines and steam turbines. Most grid-peaking power plants and some off-grid engine generators use natural gas. Recently, methane from coal mines has been successfully converted to electricity.

2. TRANSPORTATION
Compressed natural gas is a cleaner alternative to other automobile fuels such as gasoline or diesel fuel. Fertilizers: Natural gas is a major feedstock for the production of ammonia, via the Haber process, for use in producing fertilizers.

3. CHEMICAL INDUSTRY
Methane is the feedstock of choice in the chemical industry for the production of hydrogen, methanol, acetic acid, and acetic anhydride. Other chemicals derived from methane include acetylene, and the chloromethanes (chloromethane, dichloromethane, chloroform, and carbon tetrachloride).

4. SYNGAS PRODUCTION
Synthetic gas, or syngas, is a gas mixture containing varying amounts of carbon monoxide and hydrogen. It can be produced by steam reforming of natural gas or liquid hydrocarbons to produce hydrogen, or by the gasification of coal, biomass, and in some types of waste-to-energy gasification facilities.

The name comes from its use as an intermediate in creating synthetic natural gas (SNG) and for producing ammonia or methanol. Syngas is also used as an intermediate in producing synthetic petroleum for use as a fuel or lubricant via the Fischer-Tropsch process.

III. Methods of Methane gas detection
1. A Portable Remote Methane Detector:
Gas distribution companies use portable instruments for detecting natural gas leaks, in support of their emergency response and surveillance services. The conventional method used to detect gas leaks involves positioning instruments in close proximity to the area to be checked. However, this can be a difficult operation and often entails lengthy inspection periods particularly in elevated or narrow locations. To overcome these difficulties, optical methods, particularly laser based methods, were studied by lots of groups in the gas industry. The laser based methods provides us with remote detection of methane leaks and thereby improves the operational efficiency and safety levels of the natural gas distribution facilities. In particular, Tunable Diode Laser Absorption Spectroscopy (TDLAS) is a promising method to lead a compact and cost-effective remote methane detector.

In previous works, the author and his research group presented a portable remote methane detector based on TDLAS. To the best of the author’s knowledge, this detector was world’s first product that is person-portable and capable of remote detection of methane leaks. In the present work, Tokyo Gas Co., Ltd. and Anritsu Corporation jointly developed a new version of the detector (Fig. 1). The author and his research group improved the user-friendliness and cost-effectiveness dramatically from the old version.

![Fig. 1 A Portable Remote Laser based Methane Detector](image1)

![Fig. 2 An Example of How Laser based Methane Is Used](image2)

**Concept of Remote Detection**
Fig. 2 shows an example of how Laser based Methane is used. The device transmits an infrared (IR) laser beam with the wavelength set at one of the absorption wavelength (absorption line) of methane. It then receives a fraction of the backscatter reflected from the target. In this configuration, the received power can be expressed by the Lambert-Beer law as use as strong an absorption line as possible. Methane has two strong absorption bands, or groups of absorption lines, centered at 3.3 μm (ν3 band) and 7.6 μm (ν4 band). However since a near infrared diode laser is used for cost effectiveness, the available laser wavelength is limited lower than 2.2 μm. Below 2.2 μm, the strongest absorption band of methane is located at 1.64 to 1.70 μm (2ν3 band).

**Wavelength Modulation Spectroscopy**
Laser based Methane has to measure very little power since it collects limited diffused reflections from a target. In a typical case, for example, it will receive as little as 100 nW from an initial laser power of 10 mW. In addition, it has to detect very weak absorptions. For example, 100 ppm of methane corresponds to an optical depth of less than 1.
than 10^{-4}. These are significant technical challenges of remote methane detection using a near infrared diode laser. To overcome them, Laser based Methane employs the second-harmonic detection of wavelength modulation spectroscopy (WMS).

2. Methane Gas detection using differential absorption

The Institute of Optoelectronics Military University of Technology developed the prototype of laser system for gas detection using differential absorption of radiation backscattered from topographic targets. Both gas lasers were excited by RF discharge. We have obtained the output power of about 10 mW for He - Ne laser for lengths of 50 cm. The presence of methane on the distance up to 50 m can be measured by using receiver optics with the diameter of 7 cm and thermocooled HgCdTe detector. The new solution is under construction. In order to increase the range of measurement Cassegrain optics with diameter of 30 cm is being prepared. Using the special construction of gas lasers with the output power of 30 mW, the measurement distance of 200 m is expected.

In case of remote monitoring, taking into account the possibility of long-range sensing, system should operate in so called atmosphere absorption windows. Comparing the typical characteristic of atmosphere transmittance with the absorption bands of methane, it can be easily found, that its fundamental absorption band of n_4 = 1306 cm^{-1} (7.66 mm) coincide with the band of strong water vapour absorption as well as that only the n_3 band (3020cm^{-1} or 3.31 mm) lies in the transmission window. Other absorption bands of methane, representing combinations or overtons of fundamental bands, for example n_3 + 2n_3 (1.3 mm), 2n_3 (1.6 mm) are very weak, with absorption strength of single percents of fundamental ones.

On the basis of complex analysis of methane absorption bands, atmosphere transmission data, available laser sources and detection systems as well as Polish technological potentials, He-Ne laser generating radiation in the 3.39 mm band was selected as measurement source (l_{ref}). This line of generation coincides very exactly with oscillation-rotational absorption line P(7) of methane. Moreover, after practical analysis of He-Ne laser generating characteristics we propose further utilisation its two single lines, namely 3.3922 mm and 3.3912 mm. The aim is to substantially increase the measurement range of methane concentrations. The line of 3.3922 mm, having a very high absorption coefficient, allows very sensitive methane concentration detection, but only up to around 2600 ppm (referring to measurement cell of 15 cm). The additional line 3.3912 mm, with several times lower absorption coefficient allows to extend the measurement range to 2x10^5 ppm (much higher than LEL - lower explosive limit). As the reference source (l_{off}), the proposal is to develop a gas laser generating wavelength of 3.5 mm. This wavelength lies so near to the measurement one (3.39 mm), that we avoid the additional influence of different atmosphere transmittance. Our experiments have shown possibility of use of RF discharge to obtain 7 mW of output power without optimisation of gas mixture and pressure, for reasonable dimensions of laser head.

The idea of proposed measurement system is shown in fig.3. Transmitted laser beams are AM modulated due to pulse RF excitation of both lasers (TTL level modulation of power sources). The small amount of lasers output powers, through beam-splitters go to detectors D2 and D3 for on-line control of the level of output power and as reference signals for data acquisition circuits. The Cassegrain optical transmitting/receiving subassembly aims laser beams to the target (area) and collects, through D1 detector backscattered radiation. After amplification, detector electronic signals are directed to the electronic part of system. The result of methane concentration measurement is calculated on the base earlier developed algorithm. The only one cause of the different signals from two wavelengths is the presence of methane.

![Fig.3. Idea of operation and the block diagram of the device.](image-url)
It should be emphasised, that utilisation of modern, RF excited lasers allows not only to increase the output powers and extend their lifetimes, but also to simplify and increase the stability of electronics (TTL level AM modulation instead of mechanical chopping). Moreover, it increases also signal energy, measurement range and accuracy.

Several methods applied for methane concentration measurements (also other gases) can be divided to groups using different criteria, among others “in-situ” - place of sampling or “stand-off” - place of gas real presence. The first group utilises mainly chemical, physicochemical and spectral methods. A big selection of portable or stationary systems is offered. The second group offers distant measurements, with typical example - lidar. This relatively low price, mobile measurement system (on the board of helicopter or van), which links DIAL and DOAS methods and capable to detect methane up to 200 m, appears to be a good supplement to existing methods.

3. Remote Detection of Methane by Infrared Spectrometry

LMLD(LED Methane Leak Detector) is an Optical Gas Leak Detection instrument for measuring the presence of methane and ethane gas. It has been developed since 2006 in our institute. The instrument relies on measuring the absorption of light by methane in the mid infrared region. A light source made by LED (Light Emitting Diode) mounted on one end, facing an optical detector located on the opposite end. The light source produces a wide range of wavelengths, including wavelength bands absorbed by methane. LEDs of the mid-infrared band, which are made from InAsSbP, provide narrow bandwidth illumination that is projected through the sample volume and then detected by a photo detector. A photo detector made by a photodiode(PD) contains a glass lens and a mirror that concentrates ray reached from a LED light source. LEDs and PDs are equipped with the function of electric thermo cooling. The power is used to supply 12V from the battery. Fig.4 owns the diagram of a whole system of methane detection system. Then concentration is computed through a procedure series: emitting LEDs, amplifying, AD converting, calculation and displaying.

Fig. 4 The scheme of the methane detection system

Fig. 5 The schematic diagram of CH4 detector.

Fig.5 shows the schematic diagram of CH4 detector and the structure of the LED transmitters and a PD receiver along with the modulator-controller. Thermoelectric elements, controlling operating temperature, are
mounted upon LEDs and PDs. The characteristics of these InAsSbP LEDs (IBSG, Russia) are as follows: The current threshold at 1kHz rate is maximum 1A. FWHM is 0.7μm. Optical power at 1A is 400μW. Quantum yield is 0.5%. Switch time is 50ns. Operating temperature is from 77 to 320K. The receiver consists of a focusing lens system and an InAsSbP pin photodiode (IBSG, Russia). The characteristics are as follow: Cut-off wavelength at 10% is 3.8 μm. Peak wavelength at > 90% is from 2.8 to 3.4μm. Responsivity at _p is 1.0-1.2 A/W. Detection sensitivity is about 3*10^9 cm·Hz1/2/W. Fig. 4, 5 show appearances of LEDs and PDs.

4. Flame ionization detector:
Flame Ionization Detector (FID) is one of the most used detectors for gas chromatography (GC). The application area is wide. For example, petrol for air planes, kerosines, are carefully analyzed with GC-FID as a routine control. The composition of the kerosines is of great importance for the energy conversion. A completely different area is packaging of food. Your take-away hamburger is wrapped in an insulating polystyrene box. During the processing of polystyrene different hydrocarbons are added to create the end-product. When polystyrene is used within food industry, it is crucial that the product is analyzed for any residues of the hydrocarbons, since they can harm the quality of the food and your health.

The GC-FID is well suited for analysis of hydrocarbons such as methane, ethane, acetylene etc., but also for organic substances containing hydrocarbons and for volatile organic compounds (VOCs). In an FID the sample undergoes a combustion in a hydrogen/synthetic air flame. Ions and free electrons are formed in the flame. The charged particles produce a measurable current flow in the gap between two electrodes in the detector. The resulting current flow is of greater strength than the signal produced by the pure carrier gas and the fuel gas flame alone. This signal differential provides information about the sample. The current is proportional to the information which depends on the composition of the separated sample. The FID is a general detector which, with extra configurations, can be used for more specific components. For example, with placing a methanizer ahead of the FID, components containing carbon can undergo a formation to methane and thereby be suited for further FID analysis. CO and CO2 are commonly analyzed this way. For determination of organic nitrogen/phosphorus compounds a different FID configuration is needed. The sample passes a heated alkali source where charged particles are formed in contact with the alkali source. This method is normally named alkali flame ionization, also named the thermionic detector and belongs to the group of detectors in which thermal energy is used as source for ionization. The abbreviation of this method is often NPD. Flame ionization detectors are extremely sensitive and have a wide range of linearity. The only disadvantage is that it consumes the sample.

![Fig 6: Gas Analysis with GC-FID](image)

An important facet of the GC-FID is the use of a carrier gas to transfer the sample from the injector, through the column and into the FID-detector. The carrier gas must be inert and may not be adsorbed by the column material. Helium or nitrogen are normally used as carrier gas with GC-FID, and sometimes hydrogen. The detector gases, hydrogen and synthetic air, serve respectively as fuel gas and...
oxidizing gas during the combustion process. Since hydrocarbon impurities, moisture and oxygen produce a greater baseline noise which has an adverse effect on the detection limit, these impurities in the detector gases should be kept as low as possible. Like all chromatographic analytical processes, gas chromatography is a relative method, i.e. calibration with a standard mixture is required, both to check linearity and as calibration for the sample

5. Methanometers in coal mines: No regular monitoring of methane is required in areas of gassy coal mines outby the mining face. Methane ignitions that have occurred in mine outby areas indicate the need to provide better protection to workers. Handheld methane monitors are now used by some miners to make periodic measurements of methane at the working face. The IYONII gas detector which is incorporated into a miner’s cap lamp and worn on a miner’s helmet can continuously provide an alarm signal whenever methane levels exceed a set level.

Tests were conducted to evaluate the performance characteristics of this methane detector by measuring response times with methane gas supplied through a calibration fixture or adaptor. Other response time tests were performed with the detector in an environmental test box. Performance was also evaluated in a full scale test gallery where face methane emission and underground ventilation were simulated. Procedures for calibration by response time measurement of the IYONII detector have been developed. In limited testing, the IYONII detector was found to reliably detect the presence of 1 percent by volume methane.

IV. CONCLUSION

Methane gas detection was pioneered in the twentieth century by coal miners who used canary birds that would pass out if there were any spike in the amount of methane in the atmosphere. Methods of methane gas detection are covered under this paper which could effectively detect the presence of methane concentration. Thus such methods have moved on from this primitive means of highlighting its presence in the air. There are now a number of methods and devices can be used for methane gas detection. Methane gas detection is very important as it is combustible, poses such a threat to human health. Methane can lead to explosions in coal shafts - the gas trapped in the rock can be released as a result of mining - and also fires in landfill sites as a result of a process known as methanogenesis. In the home, methane is found in the natural gas used for cooking. There is also a risk of methane leaking into your home from sewer pipes. The methods covered under this paper could prevent dangerous explosions by intimating the methane presence. These methods are excessively used in industries, estimating leaks in pipe-lines, coal mines, etc.

REFERENCES


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