Innovative Technologies for Detecting Methane in the Atmosphere

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Keywords: Extreme environmental conditions, habitat, sustainable architecture, physical and climatic parameters.

Abstract: The article is devoted to the actual problem of the formation of sustainable architectural objects for extreme living conditions, caused by physical and climatic parameters. It has been established that globalization, the acceleration of the pace of scientific and technological progress, the growth of the global population and the increasing pressure on the environment caused by these factors lead architects, engineers and researchers to the need to quickly respond to changing conditions and form a favorable artificial environment in extreme environments, which are determined by physico-climatic, anthropogenic physical and socio-economic parameters. The purpose of the study is to identify the principles of the formation of architectural objects in extreme conditions in the context of international architectural and engineering trends. The methodological approach to the study of this issue is based on system analysis and is based on the materials of implemented and designed buildings and structures, as well as the study of open scientific research. The materials of the article can be used for the theory and practice of the formation of an artificial environment for extreme living conditions.

1 INTRODUCTION

It is impossible to imagine the life of modern society without achievements in the field of analytical chemistry. Accurate and timely analysis of various compounds is required in the fuel industry, agriculture, pharmaceuticals, food industry and many other industries. Chemical analysis of gaseous substances acquires a special role and importance. In the gas industry enterprises, air cleanliness and gas leaks in pipelines are constantly monitored, engineers talk about "hydrogen energy", experts in the field of transport are developing environmentally friendly fuel for rockets, airplanes and cars based on methane.

2 SCIENTIFIC AND LITERARY REVIEW

The problem of determining the composition of the gas mixture becomes particularly relevant in the light of testing hypotheses about climate change and natural gas leaks during production and transportation.

Climate change research

Questions about global warming have been the subject of scientific discussions for a number of years. According to some estimates (Lal, 2008; Schrader, 1995; Degler, 2015; Elger, 2019; Kohl, 1989; Stuart, 2005; Mizaikoff, 2013; Wilk, 2012; Glöckler, 2020), global surface temperatures have increased by about 0.88°C since the end of the 19th century.

Terrestrial ecosystems have been a source of atmospheric carbon dioxide since the dawn of agriculture, and methane since the domestication of cattle and the cultivation of rice fields. Increasing the concentration of carbon dioxide in the atmosphere enhances the effect of fertilizer. The restoration of degraded ecosystems and the combination of carbon cycles with nitrogen and phosphorus increases the carbon stock in terrestrial ecosystems.

Based on the above, it can be concluded that the validity of climate forecasts depends on the accuracy of measuring the concentration of carbon dioxide and methane.

Natural gas leaks

Methane is the main component of natural gas. Methane emissions can be the result of equipment malfunctions such as pipe cracking or leaky pipe

Mustafin, R., Bogdanov, M. and Khisamov, R.
Innovative Technologies for Detecting Methane in the Atmosphere.
DOI: 10.5220/0011569000003524
In *Proceedings of the 1st International Conference on Methods, Models, Technologies for Sustainable Development (MMTGE 2022) - Agroclimatic Projects and Carbon Neutrality*, pages 227-233
ISBN: 978-989-758-608-8

connections, emission methods such as flaring, or accidental emissions during normal transportation, storage and distribution operations (Glöckler, 2020). In addition, methane emissions from wells can be caused by loss of integrity of natural gas due to defective sealed casing pipes, cement wear in boreholes or transverse migration along neighboring geological formations (Fortes, 2014). Methane released as a result of leakage through wells and equipment accounts for 8.5% of greenhouse gas emissions in Canada (Fortes, 2014; Dosi, 2019). Methane emissions from the global transportation of liquefied natural gas account for more than 5% of the total 932 million tons of CO_2 equivalent. Average methane emissions from oil and gas wells in Pennsylvania reach 55,600 tons per year. In northeastern British Columbia, where shale gas basins are located, 75,000 metric tons of methane were released per year.

3 MATERIALS AND METHODS

Methane (CH_4), a combustible gas that has neither smell nor color, is the main component of natural gas (Aldhafeeri, 2020). It is used as a fuel worldwide as a source for electricity generation and heating and plays a significant role in climate change. Methane is a powerful greenhouse gas (GHG) with a global warming potential 28 times higher than that of carbon dioxide (CO_2) over a 100-year period (Aldhafeeri, 2020). Since the beginning of the industrial revolution, the concentration of methane in the atmosphere has increased dramatically from about 800 parts per billion (ppb) in the early 1900s to more than 1800 parts per billion in 2016. This increase can be explained, first of all, by the following anthropogenic sources of emissions: landfills, livestock waste, coal mining, petrochemical production, as well as oil and gas distribution and production facilities (Aldhafeeri, 2020). In addition, methane ignites and can be explosive if its concentration reaches 5-15% indoors (Aldhafeeri, 2020). Despite its negative impact on the environment, natural gas is valued for its abundance and clean combustion process, and therefore it will be widely used in the future (Aldhafeeri, 2020). It replaces coal due to lower CO_2 emissions in the process of combustion and lower production cost (Stuart, 2005). Moreover, it is predicted that in the future natural gas will become the second most used source of energy (Aldhafeeri, 2020).

Since the use of natural gas in the future is inevitable, it is necessary to develop solutions to reduce methane emissions.

To detect leaks in the natural gas infrastructure, it is necessary to develop reliable and cost-effective methane detector sensors. This will allow pollutants and law enforcement agencies to detect and eliminate leaks in a timely manner. Therefore, many methane sensors have been developed, each of which has its own technology. Sensors based on different physical principles are used to detect methane, for example: optical sensors, capacitive sensors, calorimetric sensors, resonance sensors, acoustic sensors, pyroelectric sensors, semiconductor sensors based on metal oxide (MOx), electrochemical sensors.

The purpose of the proposed work is to describe some new approaches in the field of methane detection. The advantages and disadvantages of these approaches, as well as various scenarios for their application, will be considered.

4 OPTICAL SENSORS

Optical gas sensors detect changes in electromagnetic waves resulting from the interaction of the analyte with the receptor (Aldhafeeri, 2020). The most common instrument for determining methane is infrared (IR) absorption spectroscopy, based on the fact that methane gas has two strong absorption lines - 2.3 and 3.26 micrometers (mid-IR range) and two weak absorption lines – 1.33 and 1.6 micrometers (near-IR range).

There are several approaches aimed at improving optical methods for detecting methane. Yang et al. (Aldhafeeri, 2020) increased the sensitivity of an optical methane sensor with a long-period fiber grating (LPFG) using a polycarbonate/cryptophane overlay with a high refractive index. The change in the thickness of the overlay led to a shift in the resonant wavelength, and at the optimal thickness, a significant increase in the sensitivity of the sensor was observed. Dong et al. improved the sensor based on the Fabry-Perot cavity (FPC) resonator to improve the accuracy of gas measurement. The technique consisted in recording the transmission maxima of the resonator modes by scanning the resonator wavelengths at each laser frequency. It was found that the FPC sensor with integrated new technology was able to achieve a methane detection sensitivity of 0.7–2.9 parts per million by mass (ppm-m). Zhang et al. developed a fiber-optic methane sensor based on graphene-doped tin oxide. The sensor was manufactured by coating optical fibers with lateral polishing with thin films of tin oxide doped with graphene, while the light source operating in the visible region was tuned to a wavelength of 1550 nm.

An interesting implementation of the optical method of methane detection is the combination of IR spectroscopy and remote chemical sensing. Yutaka and his collaborators (Matsumi, 2016) have developed a method for measuring methane by the open optical path method by detecting the second harmonic, using a near-IR diode laser for IR absorption spectroscopy. During field measurements in rice fields in India, the laser beam is returned by a reflector located tens of meters from the device and detected by a photodetector in the device (Figure 1). The measurement error at a distance of 50 m was 2%.

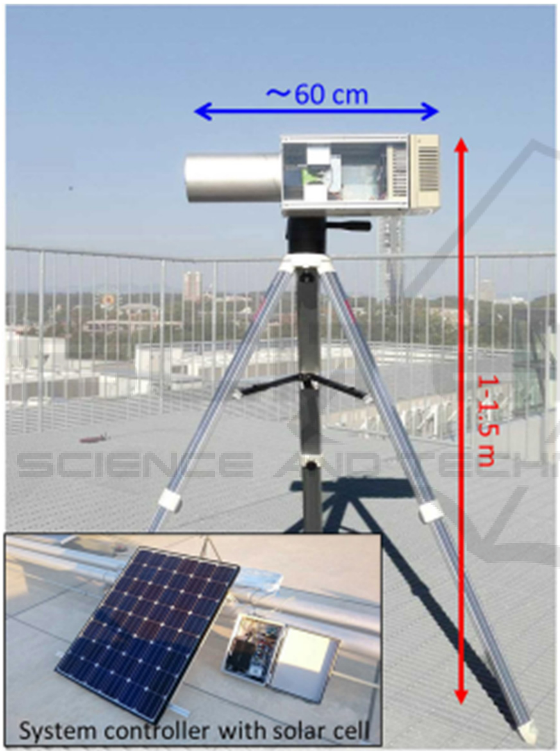

Figure 1: A field system for measuring methane concentration (CH_4) using a LaserMethane miniG detector (LMm) and a solar power source (Matsumi, 2016).

5 CALORIMETRIC SENSORS

Calorimetric sensors are used to detect methane and other combustible gases in coal mines, drilling rigs, oil refineries, and landfills (Aldhafeeri, 2020). There are three types of calorimetric sensors: a catalytic gas sensor, an adsorbent-based gas sensor, and a gas thermal conductivity sensor. A calorimetric gas sensor often consists of a temperature meter, a catalytic combustion chamber and a heating element. The principle of operation of a calorimetric sensor is based on the fact that a chemical reaction or a physical adsorption process absorbs or releases heat. The most important part of the calorimetric sensor is the material that interacts with the gas. The surface layer is often used as a combustion reaction catalyst to reduce the combustion temperature. Platinum (Pt), palladium (Pd) and rhodium (Rh) are the most commonly used catalysts in calorimetric gas sensors. Conventional calorimetric sensors use a catalytic coil made of platinum or palladium, also known as a pellistor. For methane, gas oxidation in contact with a catalyst is an exothermic reaction with the release of heat. This leads to a change in the temperature of the catalytic surface due to a chemical reaction, which is used by calorimetric sensors to obtain a useful signal.

Calorimetric gas sensors are simple, cheap and convenient to use. These sensors are affected by temperature, pressure and humidity, however, they are sensitive to methane and other hydrocarbons.

Purely calorimetric methane sensors have a measurement error of 5%. Calibration using gas with a known concentration is proposed to increase accuracy.

6 PYROELECTRIC SENSORS

Pyroelectric sensors register electromagnetic radiation at a certain wavelength range. They convert electromagnetic or thermal energy into electricity. They are non-contact thermometers operating at room temperature. In the sensor, the dielectric is located between two electrodes. The advantages of the pyroelectric methane sensor include its ability to work without oxygen, good sensitivity and a wide operating range. These sensors can operate at room temperature. In addition, the pyroelectric effect is a thermal process in which no chemical reactions are involved, so the risk of degradation of the sensor is reduced. However, pyroelectric sensors are expensive and require a high-energy power source and a constant source of heat or infrared radiation, which makes them unsuitable for many applications. In addition, they are difficult to manufacture, since a thin pyroelectric element must be fixed on a supporting base.

Dong et al. have developed a multi-gas sensor system that uses one broadband light source and several pyroelectric sensors for carbon monoxide, carbon dioxide and methane using time-division multiplexing (TDM) technology. A rotating system based on a stepper motor and a spherical optical mirror with a single reflection have been developed and integrated to improve the detection of multiple gases. Experimentally, it was determined that the detection limit of methane is 2.84 ppm.

7 SENSORS BASED ON METAL OXIDES MOX

Sensors based on metal oxides are attracting more and more attention of analytical specialists (Glöckler, 2020). The principle of operation of such devices is based on the reactions of transformation of target molecules on their semiconductor surface. Johannes and his collaborators (Glöckler, 2020) combined two optical sensing methods - luminescence quenching for molecular oxygen and infrared spectroscopy for carbon dioxide and methane to study the behavior of a sample of a semiconductor MOx sensor of methane integrated into a small volume gas cell. As a result of the experiments, it became possible to quantitatively control oxygen consumption, as well as the formation of carbon dioxide as a result of the methane conversion reaction during the operation of the MOx sensor. The latter was analyzed using a gas analyzer in the mid-infrared range, based on the technology of a hollow waveguide integrated into the substrate (substrate-integrated hollow waveguide, iHWG), in combination with a portable infrared spectrometer with Fourier transform, which can not only determine the amount of carbon dioxide released, but also the consumption of methane during the operation of a MOx sensor. This approach made it possible to quantify organic compounds (CH_4) in real time in traces. The use of chemical-resistant gas sensors based on semiconductor metal oxides makes it possible to detect explosive gases such as propane and toxic gases such as carbon monoxide or nitrogen dioxide, to detect gas leaks in atmospheric conditions and identify volatile organic compounds. This approach can be used in agriculture, automotive industry, indoor air quality control and monitoring of gases in the environment. The disadvantages of MOx sensors include limited selectivity, the advantages are small area, fast response and cost-effectiveness compared to traditional analytical methods, such as gas chromatography combined with mass spectrometry (GC-MS) and infrared Fourier transform spectroscopy (FTIR) using bulky multi-pass gas cells.

MOx sensors consist of a substrate equipped with electrodes (for example, ceramic Al_2O_3), which is covered with a sensitive layer. The electrodes allow analyzing changes in the conductivity of the sensitive layer. In addition, resistive heaters are integrated into the sensors, which are electrically separated by an insulating shield from the sensor, which later allows heating the measuring electrode in the range of 200-400 °C. Heating of the sensor layer increases the sensitivity of MOx sensors due to the higher conductivity of the semiconductor and faster adsorption/desorption of target particles on/off the surface.

Studies of SnO_2 surfaces have shown that methane oxidation occurs during several intermediate stages compared to acetate before complete oxidation to water and carbon dioxide. Acetaldehyde could be detected both on the surface and in the gas phase. However, these reactions do not proceed in the same way on all SnO_2 surfaces.

The surface structure and alloying impurities along with the layer thickness play an important role in surface processes. Temperature probably has a big influence on the type of absorption and other surface reactions that occur. The initial oxygen adsorption is largely determined by the surface temperature of the MOx sensor. In addition, humidity plays a significant role and worsens the characteristics of the device. For example, deoxidization of SnO_2 in a humid environment directly correlates with the formation of surface hydroxyl groups. The target molecules also react with the oxygen of the crystal lattice, which makes it difficult to study the change in resistance depending on the oxygen concentration.

The registered MOx sensor signal indicates a change in the resistance of the sensitive layer, which is caused by the oxidation of methane by previous adsorbed oxygen forms on the surface by a rather complex mechanism, eventually with the formation of carbon dioxide (CO_2) and water (H_2O). The resulting carbon dioxide, together with the remaining methane, can be detected using infrared spectroscopy.

As a detector, the TGS2611-C00 sensor is often used - a semiconductor thick-film sensor consisting of tin oxide SnO_2, designed to detect flammable gases in the air. According to the manufacturer's passport, the TGS2611 sensor has a high sensitivity to methane, propane and butane with a similar sensitivity. These properties are determined by the characteristics of the SnO_2 surface and the presence of impurities acting as catalysts. The thermistor was made of RuO_2, the lead wires were made of Pt - W alloy, and the connections to the sensor substrate were Ni - Fe contacts (50%). SnO_2 is an n-type wide-band semiconductor. The advantages of SnO_2 include high sensitivity and resistance to a reducing atmosphere,

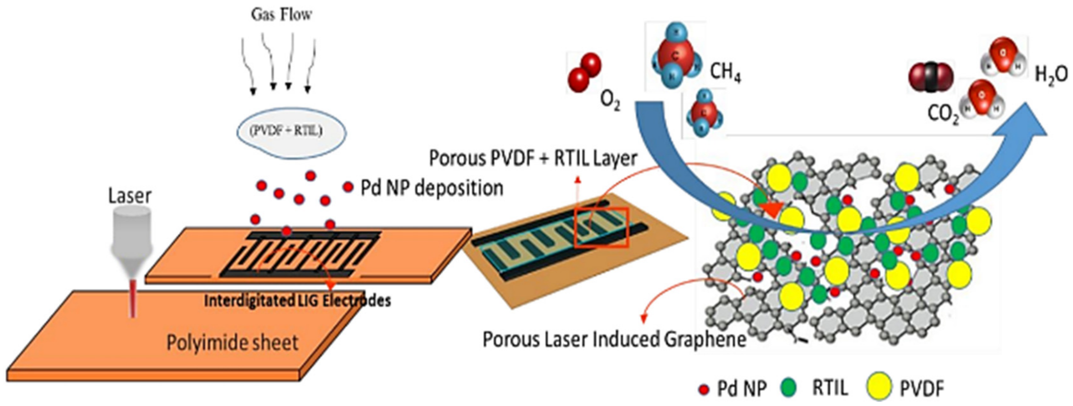

Figure 2: MOx sensor gas cell. a - an aluminum block with a gas channel (iv) and a MOx sensor (v), b - an open iHWG with an upper substrate (vi), a base substrate (vii), windows from BaF 2 (viii) (Glöckler, 2020).

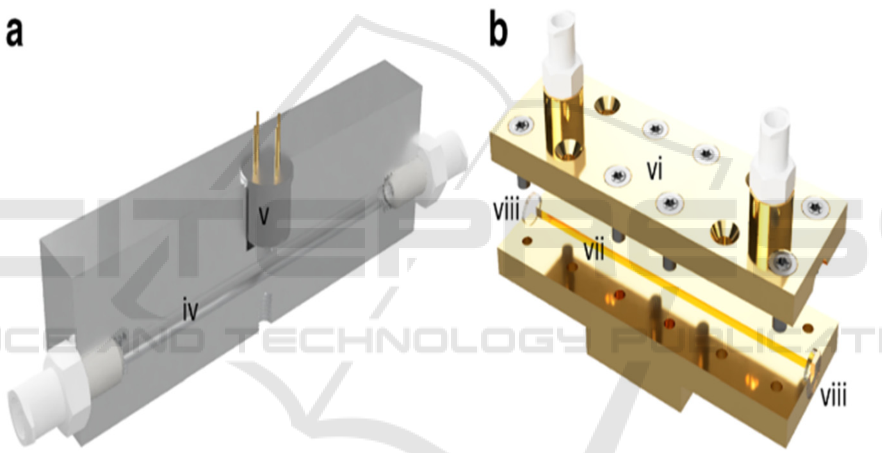

Figure 3. Diagram of the manufacturing process of an electrochemical methane sensor.

and its disadvantages are low selectivity and dependence on humidity.

Figure 2 shows a sensor circuit based on SnO_2.

The MOx sensor allows simultaneous real-time measurements of methane, carbon dioxide and oxygen using the principles of orthogonal direct optical sensing - infrared radiation and luminescence. The detection limit of methane is 41 ppm (parts per million).

8 ELECTROCHEMICAL METHANE SENSORS BASED ON LASER-INDUCED GRAPHENE WITH A SOLID POLYMER ELECTROLYTE

Manan Dosi and his collaborators (Dosi, 2019) have developed an electrochemical gas sensor that allows detecting methane at room temperature for 40 seconds in concentrations of less than one part per million. The sensor was manufactured as follows. Porous electrodes made of laser-induced graphene (LIG) form a pattern in polymer films and are impregnated with a dispersion of palladium nanoparticles to distribute the electrocatalyst inside a carrier with a large surface area. An ionic liquid in a pseudo-solid state / polyvinylidene fluoride electrolyte is applied to a flexible element to form a porous electrolyte inside a porous electrode made of laser-induced graphene, which simultaneously promotes rapid gas transfer and electrooxidation of methane at room temperature (Figure 3). The gas analyzer thus obtained is an amperometric sensor. Its ability to detect methane is tested in the presence of moisture and interfering gases.

A CO_2 laser is used to transform a polyamide sheet into a patterned graphene structure. Pd nanoparticles are absorbed into the structure of laser-induced graphene (LIG) with a large surface area, after which a porous layer of polyvinylidene fluoride (PVDF) / ionic liquids operating at room temperature (room temperature ionic liquids, RTIL) is applied to the electrodes. This provides a large number of three-phase contacts between gas, Pd and RTIL, which ensures high sensitivity and fast response (Dosi, 2019).

The described device is a flexible flat device of a small area (~ 2 cm^2), the voltage consumed is 0.6 V, the current consumed is 1.1 µA, the methane detection limit is ~ 9 ppm.

For a long time, most analytical instruments were cumbersome, expensive and time-consuming to maintain. However, recent advances in materials science, microelectronics, communications and data analysis make it possible to implement several very interesting scenarios. Let's look at some of them.

Wireless electrochemical platform based on RFID technology. Radislav Poteryailo from General Electric has proposed an interesting solution designed for the analysis of multicomponent mixtures, having a small size, low price, high selectivity, sensitivity at the level of ppm units and does not require energy (Potyrailo, 2012). The device works as follows. As you know, passive tags with radio frequency identification consist of an antenna, a microprocessor, a transmitter and a memory on which service information is recorded. Separately, I would like to note the fact that such devices do not need power supply. For the first time, this concept was implemented by Lev Semenovich Termen, who developed radio microphones for the NKVD in the 30s. The energy is taken from an external source of electromagnetic radiation, which induces induction EMF on the antenna. At the same time, the capacitor is charged. Its charge is enough to operate the transmitter. Radislav Poteryailo opened the passive RFID tag (Figure 4) and placed the nafion material on the antenna surface.

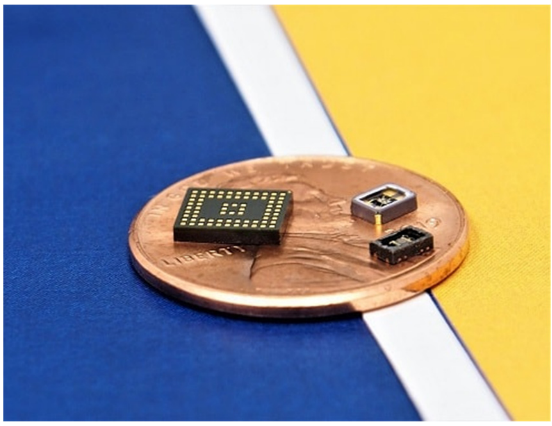

Figure 4: The multi-gas sensor is located on an American one-penny coin. https://www.ge.com/research/newsroom/ge-researchers-demonstrate-grain-size-gas-sensor-bloodhound-sensing-capabilities-ideal

9 RESULTS AND DISCUSSION

The development of materials science, communications, nanotechnology, and data analysis makes it possible to implement very interesting scenarios in the development and application of chemical sensors for detecting methane in the atmosphere. The wireless electrochemical platform has already been mentioned above. To control the ecological environment, a wireless sensor network can be deployed. A number of companies are developing chemical sensors that can be embedded in cell phones, flexible and stretchable sensors are being developed, work is underway in the field of "sensitive skin" for cyborgs, advances in micro/nanoelectromechanics are designed to create an "electronic nose".

10 CONCLUSIONS

Methane plays a very important role in the life of society. First of all, this concerns the fuel and energy complex. Thermal power plants running on natural gas are much more environmentally friendly than thermal power plants running on fuel oil or coal. In Russia, the transition of trucks and commercial vehicles to methane is a reasonable alternative to electric vehicles. Methane is the most important greenhouse gas, which makes it relevant to research in the field of anthropogenic impact of methane.

Timely and accurate detection of methane emissions into the atmosphere is an urgent problem.

This is important both for fire safety and for reducing losses in the fuel and oil and gas industry, protecting the environment and preserving the climate balance.

There are classical methods for detecting methane, such as gas chromatography or mass spectrometry. Recently, optical, colorimetric, and pyroelectric methods for detecting methane have also become widespread. Sensors based on metal oxides and electrochemical methane sensors based on laser-induced graphene with a solid polymer electrolyte are being developed (Blair, 1991). Such methods will make it possible in the future to create fairly compact, inexpensive and sensitive methane sensors. There are new scenarios for detecting methane, for example, remotely. The team of authors, together with colleagues from related industries, is ready to conduct scientific research with the above-mentioned high-tech equipment and devices.

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