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Sensor-Based Methods of Ecological Monitoring of Sulfur-Containin Pollutants in Atmosphere

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Abstract: Oil and gas industry, an important and overarching component of Russian economy, creates critical safety problems. One of the key safety issues is related to sulfur-containing oil and gas compounds. The latter particularly include hydrogen sulfide and thiols (mercaptans) that are Hazardous Chemicals (HC) and Top-Priority Air Pollutants (TPAP) on their own. Combustion of these compounds produces sulfur dioxide which is also both HC and TPAP. Thus, it is vital to search for methods and means to control the content of these substances both in the atmosphere and in the processing and the fuel gas, used at the gas and the oil extraction facilities as well as in natural gas and oil chemistry. We analyzed new rapidly developing sensors for determination of concentrations of various trace constituents in gas media. These technological tools, based on solid state gas sensors of different types, bear promising advantages for the task of measuring concentrations of sulfur-containing gas impurities both in the atmosphere and in the processing media. Concucion current study describes the most common sensors for sulfur-containing gas substances. These sensors implement electrochemical cells with solid-state electrolyte, metal oxide and traditional silicon semiconducting materials and structures, mass-sensitive piezo-quartz cells, running on surface or volume waves, passive and active optical elements. We evaluate static and dynamic qualities of these sensors as well as their consumer properties.

Key words: Sensor, gas analysis, petrochemistry, ecology, TPAP, hydrogen sulfide, mercaptans, sulfur dioxide

INTRODUCATION

Oil and gas industry is one of the most important components of the Russian economy. Therefore, the issues of optimization of this sector of economy and improvement of its functioning are of great significance. One of the most crucial problems of this branch is safety which in this case, has multiple vectors and can be separated into the following components. Based on the location of hazards:

- Extraction and primary treatment of oil and gas,
- Transportation
- Direct use and/or advanced processing of petroleum

Based on the type of hazards:

- Health and environmental
- Fire and explosion

All these constituents have individual criteria to distinguish between safe and hazardous conditions. Analyzing the situation in a certain economy field, one should consider its scale. The > 500 million tons of crude oil are extracted in Russia every year. Moreover, about 700 billion m^3 (or approximately, 500 million tons) of natural gas are annually extracted in Russia, These enormous amounts of products contain various impurities and hazardous components.

Oil has the following composition (by weight): 82-87% of carbon; 11-14.5% of hydrogen; 0.01-8% of sulfur; 0.001-1.8% of nitrogen; 0.005-1.2% of oxygen, etc. Oil contains over 50 elements in total (Gubkin, 1975) Concentrations of the listed compounds and contaminants varies in a wide range in the products of different deposits, therefore the average chemical composition of oil is tentative. As one can see the basic components of oil are not surprisingly, carbon and hydrogen. The third major element of oil is often sulfur. Furthermore, oil grades with high content of sulfur are very common in Russia. At the same time, the presence of sulfur either in crude oil or in its products is extremely disadvantageous. Similar analysis of natural has leads us to the following conclusions. Methane, an elementary hydrocarbon, constitutes the major proportion of natural gas-from 70-98%. Apart from that, natural gas may contain

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heavier hydrocarbons, homologous to methane: ethane, propane, butane as well as other substances: hydrogen, hydrogen sulfide, carbon mono and dioxide, nitrogen, helium and other impurities (Sokolov, 1972).

As long as pure natural gas is colourless and unscented, small portions of odorants-substances with strong unpleasant smell, mostly thiols (mercaptans) are deliberately added to natural gas to detect leaks. Ethanethiol, a typical odorant is added to the utility gas in quantities of approximately 16 mg per 1 m^3.

Therefore, sulfur-containing substances, primarily including hydrogen sulfide and methane and ethanethiols, are among the most unfavorable and significant impurities of oil and gas. Sulfur dioxide should be added to this list of the sulfur-containing substances as it is one of the Top-Priority Air Pollutants (TPAP), though it is not a considerable admixture in oil and gas. This substance is emitted into the atmosphere particularly due to combustion of oil products and naturl gas, if the latter contain sulfur compounds. Other sources of sulfur dioxide include metallurgical production, coal-steam plants and volcanic activity of the Earth.

MATERIALS AND METHODS

Electrochemical sensors: This technology is based on the fact that voltage-current characteristic of an electrochemical cell depends on the concentration of the detected component of the gas mixture. These sensors are subdivided into the liquid-electrolyte and the solid-electrolyte types, based on the physical state of the electrolyte. Use of various conductive media such as solutions of sulfuric acid, allows to detect hydrogen sulfide in the range of concentrations of (0.5-1000) mg/m^3 (Alsano and Satoshi, 1990). However, solid-electrolyte electrochemical sensors are more commonly used, mostly because of higher consistency of the analytical characteristics over time. By varying the composition of the implemented solid electrolytes, one can regulate the detector sensitivity, selectiveness and in some cases, response rate. Solid-electrolyte electrochemical cell with a sensitive electrode, containing gold and carbon catalyst layer, provides high selectiveness for hydrogen sulfide and ethanethiole in the presence of carbon dioxide.

The major disadvantages of electrochemical sensors are the variations in calibration curves under different temperature conditions, gradual electrolyte poisoning and sensor degradation and in some cases, high operation temperatures of the sensor.

Thermometric sensors: The working principle of thermometric sensors is based on the thermal effects of the chemical reactions between the substances of interest at the sensor surface. If the heat of the catalyzed reactions at the active centers of the sensor is used the thermochemical sensors of this kind are called thermocatalytic. They can be used to detect hydrogen sulfide in the range of 0-100% vol. concentration. Platinum is commonly used as a catalyst embedded in the active material of the work electrode (Peregud, 1978). High working temperatures (approximately 500°C) and low selectivity are the drawbacks of these sensors. That is why they are more often used for leak detection (Mierzwinski and Witkiewicz, 1989).

Semiconducting sensors: The working principle of the semiconducting sensors is based on the alteration of the semiconductor electrical conductivity due to adsorption of the detected gas on its surface or in its volume. Semiconducting sensors are usually categorized by the sensor material and are subdivided into the sensors, based on the metal-oxide or on the organic semiconductors as well as on the silicon MOS and p-n-structures (Stetter, 1978).

Tin dioxide (SnO_2) (Dramlic and Vulokic, 2001), zinc dioxide (ZnO_2) (Liaw *et al*., 1991), tungsten trioxide (WO_3) (Xu *et al*., 1999) are used in metal-oxide semiconducting hydrogen sulfide sensors. Pure metal oxides are not stable enough in the course of time and have low selectivity. These flaws can be reduced with addition of alloying agents to the initial semiconductor (Williams, 1991). The technique of creating a layer for H_2S detection is an example of the improvement of the sensor properties. Study suggests SnO_2 doping, increasing the hydrogen sulfide detector sensitivity and selectivity. Previously developed semiconducting sensor of hydrogen sulfide and ethyl mercaptan, based on WO_3 with gold alloy, has the H_2S detection limit of 20 ppb and the C_2H_5SH detection limit of 30 ppb with the sensor working temperature equal to 300 and response time of 2-3 min. Special aspects of sensor manufacturing and creation of the gas-detecting layer by the sol-gel method including the hydrogen sulfide sensors are described by Meshkova.

Semiconducting sensors, based on the Organic Semiconductors (OSC), offer the possibility of detecting sulfur compounds in gas media with the lower threshold of 10 ppb. OSC sensors, based on the polyaminoquinone-copper (II) complex have been developed for the analysis of ethyl mercaptan. Field transistors, capable of detecting hydrogen sulfide, can be created on the base of the silicon MOS-structures (Nikolaev *et al*., 2004). Hydrogen sulfide sensors, implementing the Schottky diodes are made on the base of Pd-Ti, Pd-ZnO, PbS-Si and Pd-SiO_2.Si structures.

Mass-sensitive sensors: This category includes piezoelectric quartz resonators, subdivided into the volume and the surface types. They can serve as a basis for detectors with different parameters including the gas-analyzing sensors, implementing the micro-weighing principle.

Threshold sensitivity of such microbalances can be as low as 10^{-12} g (Malov,1989) Volume-type resonators usually have frequencies up to 20 MHz. Sensors, based on the Surface Acoustic Wave (SAW) piezoelectric quartz resonators, operate at frequencies of 150 MHz and higher (Wiess,1989). Detection limit of the hydrogen sulfide SAW sensors is approximately 100 ppb. Sensors, based on the piezoelectric resonators, usually have working temperatures, close to room temperature, frequency output signal and small size. Sensitivity, speed and selectivity of such detectors entirely depend on the properties of the sensitive coating of the device.

Optical sensors: This is an extensively studied type of solid gas-analyzing sensors (Gundelach,1987). The interest in these devices can be explained by their main features: they are totally non-explosive and nonflammable their working temperatures are close to room temperature their power consumption is low (Wolfbeis, 2000).

There are two major types of optical sensors: active and passive. The sensors of the passive type lack the sensitive coating. Their main advantage is the absence of the stage of adsorption and desorption of the analyzed gas by the sensitive layer the feature which dramatically improves the response rate. The major drawback of these sensors is low selectivity in the presence of interfering gas and aerosolic impurities.

Active sensors have the detecting layer, containing the reagent, entering into a specific reaction with the analyzed gas. Among the detecting substances, most commonly used in the hydrogen sulfide active optical sensors are: leuco bases of thiazine and oxazine dyes (Vartanyan, 1955); bis-chelate complexes of heavy lanthanides with organic ligands like tetrabenzoporphyrin or tetrabenzoazopor firin, substituted polyaniline with immobilized urease; leuco form of crystal violet (Verma and Gupta, 1996). Just like in the piezoelectric resonators, sensitivity, speed and selectivity of the active optical sensors entirely depend on the properties of the sensitive coating of the device.

RESULTS AND DISCUSSION

Table 1 summarizes the major parameters that describe certain components of hazards of the previously listed substances (Shirokov, 1995). Moreover, the data on the flammability thresholds include the reference weight concentrations to facilitate the comparison with the MPC values.

Hydrogen sulfide is an explosive and toxic gas, categorized as one of Hazardous Chemicals (HC). People stop sensing this gas in the air at the concentration of 225-300 mg/m^3 while the levels of 1500-3000 mg/m^3 lead to respiratory failure. Moreover, hydrogen sulfide is a highly corrosive gas, creating difficulties in working with the media, containing it. Ethanethiol is an explosive and toxic gas, categorized as HC. Its odour threshold is 0.19 mg/m^3. The concentration of 16 mg/m^3 does not lead to any dramatic consequences even after hours-long exposure. Harmful concentration is 2200 mg/m^3.

Sulfur dioxide is a non-explosive, nonflammable, toxic gas, categorized as HC. High concentrations of this gas in the air lead to asphyxia and acute pulmonary edema (Shirokov, 1995). Moreover, sulfur dioxide as well as hydrogen sulfide is a highly corrosive gas. Given the previously mentioned numbers, we should define the standards for the detection limits of the sensors for these gases. Considering sulfur dioxide the task is simple as this gas is non-explosive and nonflammable. Therefore, the requirements for the detection limits of the sulfur dioxide sensors are clear, based on the relevant MPC. In case of the former two substances we face a dilemma. On the one hand, there are health and environmental safety regulations, expressed as various MPCs. On the other hand, there are requirements for fire and explosion safety. The previously mentioned numbers are clearly incomparable. Even MPCwa is almost four-order smaller than LFL let alone MPCda. It means that either the tools for determining concentrations should have an operational range of 4-6 orders or we should have several different tools for determining concentrations, each with its own operational range. The second option seems to be more prospective as developing a measurement tool in general and especially a gas analyzer with more or less linear measuring range, covering 4-6 orders of magnitude, is a sophisticated task.

Table 1: The Mojor parameters characterizing the hazards of certain sulfur-containing substances

Chemical compound	Hazard class	MPCwa (working area mg/m^3)	MPCste (shor-term exposure limit mg/m^3)	MPCda (daily average mg/m^3)	LFL, % Vol. (g/m^3)	UFL, % Vol.
Hydrogen sulfide	2	10	0.008	-	4.5 (65)	45.0 (650)
Ethanethiol	3	1	5.10^{-5}	-	2.8 (77)	18.2 (480)
Sulfur dioxide	3	10	0.5	0.05	-	-

Therefore, at the places of oil and gas extraction and primary treatment, MPCwa-due to general isolation of these locations from the populated areas and LFL-due to poor development of these facilities and increased probability of leaks and accidents are the most relevant parameters to use. In case of the places of direct use and/or advanced processing of petroleum we consider MPCste and MPCda to be the most important characteristics due to the large scales of operation and proximity of the plants to large and very large populated areas. LFL is also relevant as fires and explosions at such facilities are absolutely unacceptable.

In case of transportation, all these criteria can be relevant, depending on the scope and the type of transport. All the aforesaid substantiates the importance of developing gas-analyzing tools which would be able to detect the required gases in different ranges of concentration. Techniques, based on the implementation of various solid sensors are among the most actively developing methods and tools for detection of sulfur-containing gases. We should now specify the meaning of the term “sensor”. We use this word to refer to an initial detecting element that transforms the properties (chemical in our case) of the examined medium into an electric or an optical signal. The electric signal can be either an amplitude or a frequency one. The optical signal is usually amplitude. Chemical sensors are commonly categorized, basing on the fundamental physical principle, underlying their functioning. The following types of sensors are distinguished: electrochemical, thermometric, semiconducting, piezoelectric quartz mass-sensitive resonators and optical (Stetter, 1978).

Improvement of life safety is an important development goal of the modern society. Industrial safety is viewed as one of the crucial components of general safety. One-time control mode is an Achiles’s heel of proper functioning (i.e., safety) of various equipment. Sure at the moments of manufacturing or periodical inspection the equipment is in working order.

CONCLUSION

However, nobody knows what happens to it during its operation or storage between the regular checks (if those are actually performed). At some point, a breakdown can happen and it is very unfortunate to discover it while removing the remnants of destroyed buildings. It is way better to detect the failures before any irrecoverable and/or very expensive consequences. In order to do that, one should equip the critical spots of the object with the tools for detecting the change in conditions, in our case in the gas composition of the surrounding space. However, traditional chemico-analytical and instrumental methods of gas analysis cannot be practically implemented in the development of multiple-point automated systems of the object control with a large number of spatially distributed sensors which in turn, should be small, power efficient, sustainable, relatively cheap and in some cases, non-explosive and nonflammable. Solid state sensors and the methods of control, based on this technology, mostly meet these requirements. Some of these sensors are used more often, some of them-less but there is an application for all of them. We are going to provide a brief description of them.

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