Using the TDLAS Method in the Spectral Range of $4860-4880~cm^{-1}$ for Online Detection of H_2S in the Atmosphere

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Currently, the constantly growing industrial production increases the amount of man-made emissions of harmful substances into the atmosphere [1-3]. The hydrogen sulfide (H₂S) – sulfurated hydrogen (H₂S) – found in the refinery products of oil and gas industries and being an accompanying gas in oil and gas production, may be singled out among such substances. Hydrogen sulfide is a hazardous volatile compound, toxic and highly flammable, with an intensive corrosive effect. Thus, upon intake of high concentrations of hydrogen sulfide by the human body, it may cause pulmonary oedema, paralysis and even death. Many accidents with hydrogen sulfide leakage are registered annually, with known fatal cases.

The above-mentioned factors determine the need for high-precision and high-sensitive online H_2S detection tools in both industrial emissions and residential areas. However, the existing gas analyzers do not allow for high-sensitive online detection. Moreover, they are often difficult to use and unreliable.

One of the promising high-sensitive H_2S detection methods may become the tunable diode laser absorption spectroscopy (TDLAS) based on the phenomenon of direct absorption of laser radiation by gas, previously implemented for some other substances, for instance, $^{13}CO_2$ [4,5]. This method is characterized by high selective ability, making it possible to resolve vibrational-rotational absorption spectra of various substances mixed together. It allows to register the absorption signals of the studied spectral absorption lines and obtain information about the concentration of the analyte in the test mixture at the level of 10^{-8} relative units.

Studies results of the H_2S absorption in the spectral range of 4860–4880 cm⁻¹ obtained by the diode laser absorption spectroscopy method, which may be implemented for the H_2S online detection in the atmosphere, are presented in this study.

The TDLAS method based experimental unit has been developed to conduct studies of the H_2S absorption in the spectral range of 4860-4880 cm⁻¹. The measuring system used a single-frequency tunable diode laser (TDL) with vertical radiation output with the possibility of smooth adjustment of the generation wavelength either in manual or automatic modes. The TDL was controlled using a specially designed laser control unit (LCU): the generation wavelength was adjusted by changing the laser crystal temperature in the range from +15°C up to +35°C, while the maximum output power of the laser was \sim 1 mW. The TDL operation mode is quasi-pulse, and the radiation modulation parameters were also controlled using LCU.

Four vibrational-rotational H_2S absorption lines belonging to the vibrational transition 021-000 were recorded while conducting experimental studies of the hydrogen sulfide.

It is necessary to determine the H₂S spectral absorption lines most promising for H₂S detection in terms of achieving the best sensitivity in order to develop a high-sensitive, a selective detection system for hydrogen sulfide mixed with other possible gases the main of which is CO₂. The main criteria for choosing such lines include, first of all, the best resolution (maximum distance) of the hydrogen sulfide absorption lines in relation to the carbon dioxide absorption lines and, secondly, the highest values of the H₂S lines absorption coefficients.

The following distances between the H_2S and CO_2 spectral lines have been determined based on the measurements results: line 1 H_2S (center frequency 4861.2 cm⁻¹) is 0.28 cm⁻¹ away from the center frequency of the closest absorption line of CO_2 , line 2 H_2S (center frequency 4864.8 cm⁻¹) is 1.31 cm⁻¹

and $0.37 \,\mathrm{cm^{-1}}$ away from the two closest central frequencies of the CO₂ absorption lines, line 3 H₂S (center frequency 4871.5 cm⁻¹) is 0.96 cm⁻¹ away from the central frequency of the closest CO₂ absorption line, line 4 H₂S (center frequency 4875.2 cm⁻¹) is 1.71 cm⁻¹ and 2.21 cm⁻¹ away from the closest central frequencies of the CO₂ absorption lines. Thus, absorption line 4 of hydrogen sulfide is the furthest from the absorption lines of carbon dioxide.

As for the second criterion, the highest value of the absorption coefficient was also found at line 4 (in the center of the line, the absorption coefficient equals to 4.79×10^{-4} cm⁻¹). Consequently, this line should be considered the most promising for H₂S detection using the TDLAS method.

Thus, the conducted studies show potential for using the TDLAS method for the high-precision and high-sensitive hydrogen sulfide detection in the atmosphere.

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