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NEW METHOD OF MEASURING HYDROGEN CONCENTRATION IN AIR

The pulsed discharge helium ionization detector (PDHID, PD-D2-I, Valco) is used to measure hydrogen concentration in air. The detection level of 10 pg (50 ppb) has been obtained. The dependence of the detector response on the mass of hydrogen was linear in the range of five orders of magnitude. The method will be used for the monitoring of hydrogen concentration in air.

1. INTRODUCTION

Due to population growth and industrialization of developing countries the world's demand for energy is still growing and probably by 2050 will be doubled. The supply of fossil fuels limited, therefore the coming generations can face serious energy crisis [1]. For this reason, recent researches are directed to another energy sources. The promising alternative to fossil fuels is hydrogen. In reaction with oxygen, hydrogen releases energy, explosivly in heat engines or quietly in fuel cells, and the only product of the reaction is water [1], [2].

The creation of energy system based on hydrogen requires an adequate technology. Hydrogen may be produced in several ways, e.g., by steam reforming, but all of them are too expensive or base on fossil fuels [3], [4]. The next problem stems from a small density of hydrogen. This feature makes its storage and transportation more difficult compared to natural gas or petrol. Moreover, hydrogen easily diffuses through different materials and can escape to the atmosphere both from vehicles and from the production installations. It is especially unsafe because its inflammable, spontaneous ignition may occur in a wide range of concentrations (2–75%). The flame is invisible,

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so the point is to construct the equipment making the detection of this gas in atmospheric air possible at its low concentration [5], [6].

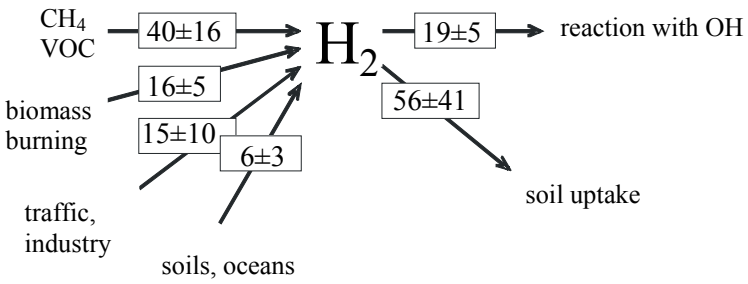

Fig. 1. The hydrogen budget in 2002 (Tg/yr) [7], [8]

The global annual budget (figure 1) is estimated at ~75 Tg/yr (million tons/year). The main source, accounting for about 50% of atmospheric hydrogen emission, is the oxidation of both methane and nonmethane hydrocarbons. The combustion of fossil fuel and biomass burning are responsible for about 40% of all the hydrogen released into the atmosphere. The other 10% is emitted from volcanoes, oceans and nitrogen-fixing legumes. Whereas the major sinks of hydrogen gas are in soil uptake (75%) and atmospheric oxidation by hydroxyl free radicals $OH^{\bullet}$ (25%) [7], [8].

In the world, the measurements of atmospheric hydrogen are carried out by several laboratories only. Since 1994 the hydrogen concentration has been measured at the Mace Head station, Ireland [9]. Based on these measurements, we can conclude that hydrogen concentration changes seasonally from 480 ppb in winter to 560 ppb in summer.

The globally averaged hydrogen concentration in 2002 was about 0.5 ppm. An average annual increase of 0.6 ± 0.1% of hydrogen per year is observed [7]. As a result of applying hydrogen technology the concentration of this gas in the atmosphere will be rising which may lead to the reduction of hydroxyl radicals ($OH^{\bullet}$) [10], [11] and the increase in methane concentration in the atmosphere. It should be stressed that methane is the next to carbon dioxide a greenhouse gas. If hydrogen is used as a fuel in a way comparable to that of fossil fuels (taking account of aeroplanes), the concentration of water vapour in the air will increase considerably. On the second hand, the use of fuel cells will restrict the emission of nitrogen oxides, carbon oxide or carbon dioxide (exhaust gas from cars), which will reduce the air pollution [11].

Photochemical reactions, which can occur in the troposphere after implementing a hydrogen technology, are not known sufficiently to define unequivocally the direction of changes, which can take place in the atmosphere. Under the circumstances the hydrogen concentration in the air ought to be continuously measured.

2. THE METHOD OF HYDROGEN CONCENTRATION MEASUREMENT IN THE AIR

In the Department of the Physicochemistry of Ecosystems, the Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, the chromatographic method of hydrogen concentration measurement in the air is developed. The scheme of measurement setup is shown in figure 2. This system consist of the pulsed discharge helium ionisation detector (PDHID, type PD-D2-I), 10-way Valco valve (V10) equipped with the sample loop connected with two chromatographic packed columns (C1, C2) working in a 'back-flush' mode. The columns (C1, C2) of 1/8' in diameter, 2 m and 3 m long respectively, are filled with molecular sieve 5A. As a carrier gas a high-purity helium 5.0 (99.999% purity) from Linde Gas AG, additionally purifying by helium purifier HP2 (Valco Imstruments), was used [12].

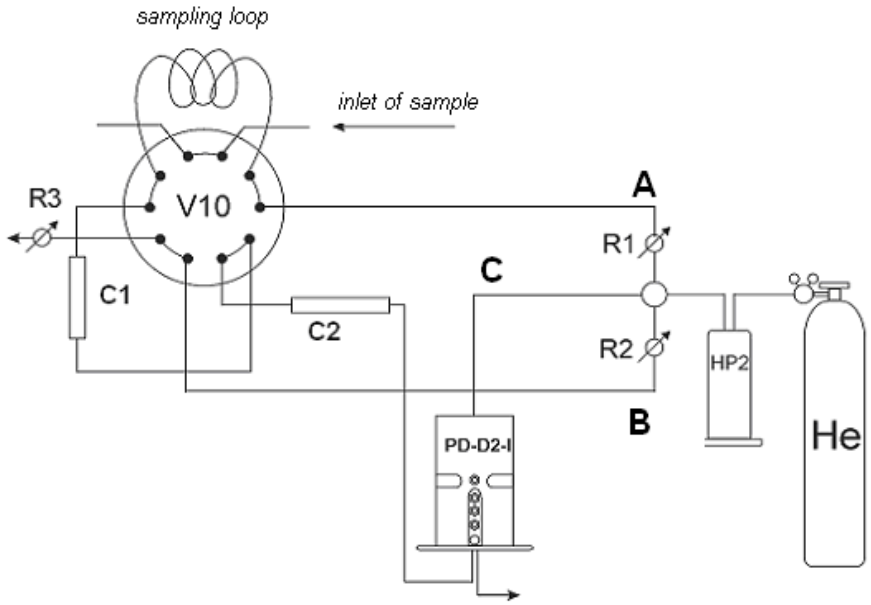

Fig. 2. The scheme of hydrogen measurement setup

The helium stream after passing through a purifier is divided into three substreams A, B, C. Two of them are used as a carrier gas, which is controlled by regulators R1, R2, whereas the third one (C) supplies a detector PD-D2-I. The sample of air filling a sample loop (see figure 2) after switching the valve V10 is introduced into the columns connected in series and injected into the column C1, where it is partly separated. At the moment neon and hydrogen leave the column C1 and are injected into the column C2, the valve V10 is switched again and the rest of gases being in the first col-

umn (oxygen and nitrogen) are removed. In the column C2, hydrogen and neon are separated, and then they are introduced into the detector. The detector signals are registered by the computer equipped with program Pick Simple (figure 3). During analyses the temperatures detector and the columns are 80 °C and 50 °C, respectively. The flow rate of a carrier gas in the detector, according to producent recommendations, is 50 cm^3/min, whereas in the columns – 18 cm^3/min. The 'back-flush' time is 100 seconds. The chromatogram of air analysis with using the sample loop V_p = 2 cm^3 is presented in figure 3. The time of the valve V10 switching is chosen experimentally. Due to changing the position of valve V10 after 100 s, we have only neon and hydrogen in column C2. This system of column change allows us to avoid the introduction of big amounts of oxygen and nitrogen into detector, which considerably limits the time of analysis.

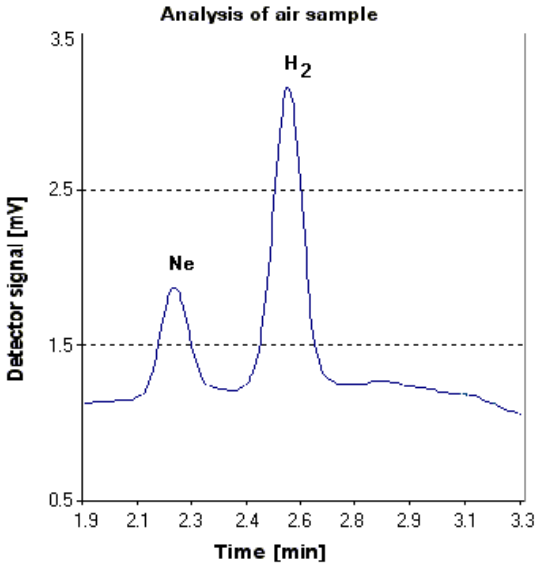

Fig. 3. The example of air sample analysis
(detector temperature of 80 ºC, column temperature of 50 ºC, sample volume of 2 cm^3, flow rate of carrier gas in the detector of 50 cm^3/min and in the columns of 18 cm^3/min)

A detector linearity for hydrogen was examined using exponential dilution method. This examination proves that the linearity of a detector characteristic is within the range of five orders of the hydrogen concentration. For an ambient air sample whose volume is 2 cm^3, the hydrogen detection level equals 50 ppb (10 pg/cm^3) of hydrogen. In a quantitative measurement, several standards have been prepared in the bottle of one litre volume. An average temporary concentration of hydrogen in Kraków approaches 0.64 ± 0.05 ppm (20 March 2006).

3. CONCLUSIONS

The developed method of measuring hydrogen concentration will be used for monitoring hydrogen in the air of southern Poland. The measurements conducted for a long time permit us to define the kind of seasonal changes of hydrogen concentrations in this region of Poland. An unknown impact of hydrogen technology on environment will be observed at the Department of the Physicochemistry of Ecosystems, the Institute of Nuclear Physics, Polish Academy of Sciences in Kraków, based on the measurements of hydrogen concentration in the GC system described above, but fully automated.

ACKNOWLEDGEMENTS

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NOWA METODA POMIARU STĘŻENIA WODORU W POWIETRZU

Do pomiaru stężenia wodoru w powietrzu został użyty detektor helowy z wyładowaniem impulsowym (PDHID, PD-D2-I, Valco). Otrzymany poziom detekcji to 10 pg (50 ppb). Zależność sygnału detektora od masy wodoru była liniowa w zakresie pięciu rzędów wielkości. Metoda będzie zastosowana do monitorowania stężenia wodoru w powietrzu.