Chromatographic analysis of a cold plasma jet generated by an electrode microwave discharge in argon flow, interacting with atmospheric air

V M Chepelev*, A V Chistolinov, S N Antipov and M Kh Gadzhiev
Joint Institute for High Temperatures of the Russian Academy of Sciences (JIHT RAS) 125412, Izhorskaya st. 13 Bd. 2, Moscow, Russia

*E-mail: chepelev@ihed.ras.ru

Abstract. Application of gas chromatography in analysis of a cold plasma jet generated by an atmospheric pressure microwave discharge in argon flow was considered. Previously developed 2.45-GHz-plasmatron with the external 6-rod-electrode plasma torch was used as a microwave plasma source. The analysis of gaseous samples showed that CO concentration increases by 5-6 times and new gaseous products appear – H2 and CH4 as a result of plasma-gas interaction. The production of CO, H2 and O2 occurs in the processes of dissociation of CO2 and water vapor in the nonequilibrium plasma through the vibrationally excited states.

1. Introduction

A non-equilibrium plasma is generated by means of various types of electrical discharges or electron beams. In this case, the main part of the electric energy goes to the production of energetic electrons, but not to heating the neutral gas. Energetic ions, in turn, stimulate certain atomic-molecular transformations and a whole spectrum of radicals and excited particles with high reactivity are produced. From the 2000s, there has been significant scientific and practical interest in the study non-equilibrium plasma due to new opportunities for their application for modification of the functional surface properties of a wide variety of materials (metals, ceramics, glass, polymer and organic materials). To this day, low-pressure glow discharges (for example, capacitive RF discharges) are used to treat various surfaces with non-equilibrium plasma [1]. However, this type of plasma is characterized by a low density of atoms and, therefore, a low frequency of collisions between electrons and heavy particles.

Recently, non-equilibrium plasma processes have been increasingly studied in atmospheric pressure discharges, which have a much higher charge density and, as a result, a greater reactivity. Particularly, self-sustained microwave discharges and their plasma jets, which lead to effective dissociation of molecules and the production of active radicals, are of great interest. Numerical calculations are performed to obtain information on the chemical composition of the plasma jet [2]. However, to date, experimental data have been obtained for only a few of the particle types [3]. In this regard, an important role is played by both the development of new and the development of traditional techniques for analyzing gas-plasma media.

One of the widely used methods of analysis is gas chromatography. Along with simplicity, it is highly accurate and uses an arsenal of different chromatographic columns and detectors [4]. Previously, we investigated the atmospheric argon plasma generated by new microwave plasma source (plasmatron) using optical emission spectroscopy. As a result, molecular bands of NO, OH, N2, NH were found in
the plasma spectra as well as electron and gas temperatures were estimated: \( T_e \approx 0.1-1 \text{ eV}, \ T_g = 1200 \pm 100 \text{ K} \) [5]. In this paper, we present the application of gas chromatography to study the production of active particles in the cold plasma jet generated by the plasmatron recently developed.

2. Experimental procedure and results

For the research, a waveguide-type microwave plasmatron with an external electrode plasma torch was used [5, 6]. The microwave plasmatron operates at a frequency of 2.45 GHz, has a microwave power in the waveguide of up to 3 kW and a power in the torch of up to several hundred watts. The plasma torch is a cylindrical discharge chamber with 6 rod electrodes inside which form a regular hexagon in a cross section. When a gas passes through discharge in the chamber, a cold plasma jet is formed behind the outlet of the torch (discharge streaming afterglow). Argon was used as a plasma-forming gas, the gas flow rate was about 7.5 standard liters per minute.

The chromatographic gas complex "Chromos GKh-1000" (Russia) was used for analysis of gaseous samples. In the chromatograph a carrier gas was fed from a cylinder through flow and pressure regulators to the chromatographic column at a constant rate. High-purity argon (99.998%) was used as a carrier gas. Gas samples were analyzed using two detectors:

- flame ionization detector (FID) designed for the determination of most organic compounds, which is an almost ideal detector for the analysis of trace hydrocarbons and most other organic compounds;
- thermal conductivity detector (TCD) designed for the analysis of compounds, the thermal conductivity of which differs from the thermal conductivity of the carrier gas. It allows to determine small concentrations of hydrogen, oxygen, nitrogen and other gases with high sensitivity.

A gas-tight 20 ml syringe device «ELCHROM» (Russia) with three-way valve was used for sampling through a hollow medical needle. It provides effective control of gas flows and constancy of the molar composition of the sample. Before each sampling, the syringe was thoroughly washed through the gas valve in the chromatograph and filled with carrier argon. Just before sampling from a given point, argon was squeezed out of the syringe and then a sample was taken. This procedure makes it possible to obtain a sample from the investigated area without impurities of atmospheric air in the needle and in the syringe outlet valve.

The following samplings were carried out (Figure 1):

- atmospheric air in the room;
- argon from the gas cylinder;
- at the point in pre-channel area (1);
- at the point in after-channel area (2);
- at the point in the cold plasma jet at a distance of about 2 cm from the torch outlet (3).

As a result of chromatographic analysis, the percentage of the following products in the studied gas samples was determined: \( \text{N}_2, \text{O}_2, \text{H}_2, \text{CH}_4, \text{CO} \text{ and } \text{CO}_2 \) (Table 1). It is clearly seen that \( \text{H}_2 \) and \( \text{CH}_4 \) appear in the discharge channel and the concentration of \( \text{CO} \) increases by 5-6 times. This effect is apparently due to the mixing of atmospheric air containing water vapor into the discharge zone. Moreover, the intensity of mixing increases at the discharge glowing. The production of \( \text{CO}, \text{H}_2 \text{ and } \text{O}_2 \) occurs in the processes of dissociation of \( \text{CO}_2 \) and the processes of direct decomposition of water vapor in a nonequilibrium plasma through the vibrationally excited states of the reactants:

\[
2\text{CO}_2 \rightarrow 2\text{CO} + \text{O}_2, \\
2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2.
\]
Figure 1. Scheme of the experimental setup. Gas chromatography was carried out for samples from (1) pre-channel area, (2) after-channel area, (3) cold plasma jet at a distance of about 2 cm from the torch outlet. Diameter of the rod-like electrodes is 4 mm, discharge gap is 4 mm, “mw” – microwave unit (magnetron and waveguide) with power supply. The inset shows the microwave discharge in the torch (view from the outlet side, gas flows towards an observer).

It should be noted that the specific feature of elementary atomic-molecular processes in a nonequilibrium plasma is that the values of translational and rotational energies are much less than the vibrational energy of molecules. For most non-electronegative molecules (N₂, CO, CO₂, H₂, H₂O, etc.), the rate of vibrational excitation by electron impact is quite high, and the main part of the discharge energy input at an electron temperature $T_e \sim 1$ eV is localized on the vibrational ground electron states [7]. This mechanism of vibrational excitation of molecules by electron impact is characterized by an important advantage – it can stimulate chemical transformations with the highest energy efficiency compared to other channels of plasma-chemical reactions.

|          | CO₂, %     | CO₂, %     | CH₄, % | N₂, % | O₂, % | H₂, % |
|----------|------------|------------|--------|-------|-------|-------|
| Ar       | 8.5·10⁻⁴  | 9·10⁻³     | 0      | 0.077 | 0.021 | 0     |
| Pre-ch   | 9.9·10⁻⁴/1·10⁻³ | 3·10⁻³/3·10⁻⁴ | 0       | 0.17/0.26 | 0.04/0.065 | 0 |
| After-ch | 9.9·10⁻⁴/6.8·10⁻³ | 3·10⁻³/1.6·10⁻³ | 0/1.3·10⁻⁵ | 0.24/0.28 | 0.058/0.069 | 0/2·10⁻³ |
| Plasma jet | 1.2·10⁻³/1.1·10⁻³ | 5.4·10⁻⁴/6·10⁻⁴ | 0/1.7·10⁻⁵ | 0.42/0.29 | 0.11/0.071 | 0/1.3·10⁻³ |
| Air      | 0.057     | 0.042      | 1.3·10⁻⁴ | 78.7  | 20.7  | 9·10⁻⁴ |
3. Conclusion
Gas chromatography was carried out for the cold plasma jet, that is discharge streaming afterglow, generated by the new electrode plasma torch of the atmospheric pressure 2.45-GHz-plasmatron recently developed. The analysis of gaseous samples showed that in the microwave discharge CO concentration increases by 5-6 times and new gaseous products appear – hydrogen and methane. This effect is due to enhanced mixing of atmospheric air containing water vapor to the argon flow in the discharge area. The production of CO, H2 and O2 occurs in the processes of dissociation of CO2 and water vapor in a nonequilibrium microwave plasma through the vibrationally excited states. The chromatographic analysis used in this work is suitable for studying carbon- and hydrogen-containing gaseous products which are poorly detected by spectral methods due to low concentrations of the products in the plasma jet. Thus, gas chromatography can complement emission spectroscopy for investigation of active particles production in non-equilibrium cold plasma jets.

Acknowledgments
The work was supported by the RFBR under Grant №19-08-00844.

References
[1] Kutepov A M, Zakharov A G and Maksimov A I 2004 Vacuum-plasma and plasma-solution modification of polymer materials (Moscow: Nauka)
[2] Naidis G V 2014 Plasma Sourc. Sci. Tech. 23 065014
[3] Lu X and Wu S. 2013 IEEE Trans. Plasma Sci. 41 2313
[4] Rahman M M, Abd El-Aty A M, Choi J H, Shin H C., Shin S C and Shim J H 2015 Chapter 3 Basic Overview on Gas Chromatography Columns Analytical Separation Sci. vol. 3 (Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim) p 823
[5] Antipov S N, Sargsyan M A and Gadzhiev M Kh 2020 J. Phys.: Conf. Ser. 1698 012029
[6] Chepelev V M, Chistolinov A V, Khromov M A, Antipov S N and Gadzhiev M Kh 2020 J. Phys.: Conf. Ser. 1556 012091
[7] Rusanov V D, Fridman A A and Sholin G V 1983 Sov. Phys. Usp. 24 447