# DYNAMIC METHOD OF GAS MIXTURES CREATION FOR PLASMA TECHNOLOGIES

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The issue of creating multicomponent gas mixtures intended for use in plasma installations is considered. A dynamic method for obtaining gas mixtures based on supercritical outflow of gases from tanks through calibrated holes. It is shown that with an appropriate choice of the volume of capacities and areas of critical holes, a high accuracy of the specified mixture composition can be ensured. If it is necessary to generate a gas mixture from components having different adiabatic parameters, it is suggested to correct the initial pressure of the gases in the tanks. This will also allow compensating for the errors associated with the manufacture of structural components of the mixture generator. As an example the calculating a mixture generator based on the proposed method is given, which confirms the possibility of providing its component composition with an error 0.01 %.

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## INTRODUCTION

Gas mixtures of various compositions are widely used in plasma coating processes: physical, chemical and plasma-assisted chemical deposition. So, for example, to create coatings of complex composition, the follow mixtures can be used: $N_2$ + $CH_4$ [10]; $N_2$ + $C_2H_2$ [10]; $N_2$ + Ar [10]. The effect of the component composition of the gas mixture used on the properties of the coatings obtained has been investigated by many authors. In particular, the effect of the component composition of the Ar-$CH_4$ mixture on the structural, optical, and mechanical properties of diamond-like coatings in the CVD process, and the effect of the component composition of the Ar-He mixture on the microstructure of the coatings in the PS-PVD process were described in the works [10] and [5] respectively.

The methods of preparing gas mixtures can be divided into two main groups: static and dynamic. The generator of gases mixture for ion-plasma technologies based on the static manometric method has been described in the work [10]. With this method, a preliminary cyclical blowing of the mixing chamber by one of the gases is carried out, then the components are fed up to the specified partial pressures. The disadvantage of this method of a gas mixture generating is an increased consumption of gas used for purging. In addition, using static methods it is difficult to achieve homogeneity of the mixture in the mixer vessel during storage, and generation of mixtures of reacting gases causes serious difficulties.

These shortcomings are devoid of dynamic methods for generating gas mixtures, the main ones of which are described in the ISO 6145 series of standards. At the same time, the accuracy of providing the component composition by using such methods today does not exceed 0.5 %. This accuracy is insufficient for many practically important cases, so the task of increasing it is actual.

## ANALYSIS OF THE STATE-OF-THE-ART AND THE PROBLEM STATEMENT

From the known dynamic methods of generating gas mixtures [7], the method of critical holes is chosen as the basic method for increasing the accuracy of the component dosing in the present work. This choice was made due to the following considerations. The main idea of this method is that when the gas flows through a calibrated hole when a critical pressure difference is reached, the volume flow through the hole stabilizes, and the flow occurs at a velocity equal to the local sound velocity. This allows to obtain the required ratio of gases in the mixture, choosing according to the diameter of the critical holes [8].

When the gas mixture is dynamically generated in vacuum chambers of plasma installations, the critical pressure differential between the gas mains and the working chamber of the installation is automatically ensured. Therefore, critical flow conditions will be satisfied in the implementation of any of the known methods, in certain cross sections of the main lines. The method of critical holes is one of the most accurate among dynamic methods of generating mixtures. In the basic variant of the method, the accuracy of dosing of components at the level of 0.5 % is ensured. Therefore, the choice of this method of generating gas mixtures for plasma technologies should be considered an obvious solution and attempt to implement this approach that were made back in the 90 s of the last century [9].

In the basic version of the method, the constancy of the ratio of the components is ensured by maintaining the equality of pressures and temperatures in front of the critical holes. Ensuring compliance with these conditions is problematic. Let us illustrate this with an example of a typical device scheme for obtaining a mixture by the method of critical holes (Fig. 1), given in the standard ISO 6145-6 [7].

In this version of the method, the pressure equalization in the gas supply networks is carried out by two reducers (3 and 15) and two pressure regulators (6 and 18). The pressure control just before the critical holes is carried out by two pressure gauges (7 and 20). All these devices can have different errors, the operation of the regulators inevitably has some (and different) delay. In addition, the hydraulic resistance of the line is 5-6-7-8, differs from the resistance of the line 17-18-19-20, at least because they contain different devices (check valve 8 and ventilating valve 19). The difference in the

properties of the gases inevitably leads to a difference in their temperatures, the passage of the pressure regulators, which directly affects the magnitude of the local sound velocity.

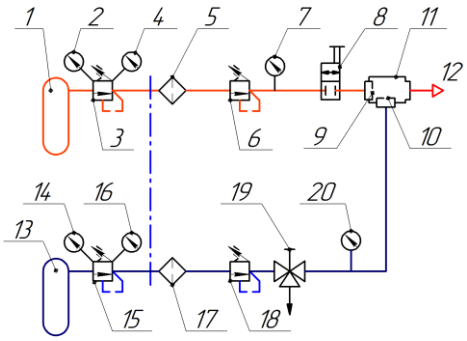


*Fig. 1. Diagram of the device for the preparation of binary mixtures by the method of critical openings: 1, 13 – cylinders with gas; 2, 14 – manometer (inlet pressure); 3, 15 – reducer; 4, 16 – manometer (delivery pressure); 5, 17 – the filter; 6, 18 – pressure regulator; 7, 20 – pressure gauge; 8 – check valve; 9 – hole (complementary gas); 10 – hole (calibration component); 11 – laughter; 12 – outlet for the calibration gas mixture; 19 – the ventilating valve*

The traditional way to improve the accuracy of the method is to calibrate manometers and critical holes, increase the accuracy of regulators, and use additional stabilizers of gas temperature [10]. As it was shown in [11], avoiding the requirement for the accuracy of dosing of the amount of a mixture, and limiting the requirement to ensure the accuracy of the ratio of the components, it is possible to increase the accuracy of the method to 0.1% during the calibration of critical holes. However, the reserves of further improvement of accuracy with the help of such approaches are almost exhausted. Obviously, to further improve the method of critical holes, it is necessary to use new technical solutions. This is the purpose of this study.

## DESCRIPTION OF THE FACTORY METHOD OF THE MIXTURE OF GASES

The proposed solution refers to the case when it is required to periodically fill the working chamber with a mixture with a specified ratio of components. In this case, the requirement to provide constant values of pressure and temperature in front of critical openings can be avoided. Instead, it is sufficient to provide the values of these parameters that would ensure a given ratio of the mass concentrations of the components. This is most easily achieved by introducing intermediate volumes of different volumes in the supply line of gases (Fig. 2).

With such solution, the supply of gases ceases after the tanks are filled and the preset pressure level is achieved. Part of the gas path after the valves 9 and 19 is evacuated together with the working chamber. Subsequently, the generation of the mixture occurs after the opening of the valves 9 and 19 accordingly in the mixer with critical holes 10.

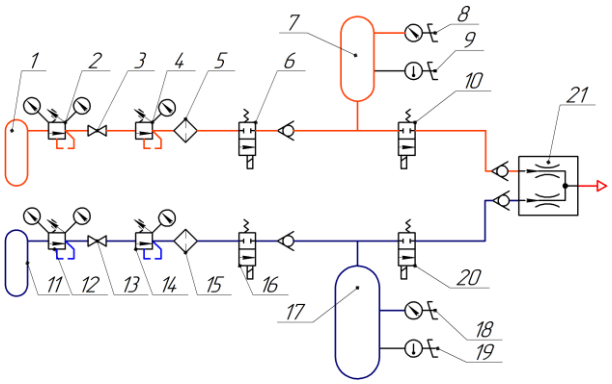


*Fig. 2. Diagram of the device for preparing binary mixtures by the improved method of critical holes: 1, 11 – gas cylinders; 2, 12 – reducer; 3, 15 – the valve; 4, 14 – filter; 5, 9, 19 – the electromagnetic valve; 6, 16 – intermediate containers; 7, 17 – pressure sensor; 8, 18 – temperature sensor; 13 – stop valve; 10 – Holes*

The gases, thus, freely flow from the tanks 6 and 16 without the use of any regulating devices. The accuracy of dosing of the components in the mixture is ensured by the appropriate selection of the areas of the critical openings, the volumes of the tanks, and the initial pressures in them.

Without loss of generality, the procedure for such a choice is considered for the case of the formation of a two-component mixture. Let it be necessary to ensure that the mass concentrations of the mixture components are equal $\beta = c_1/c_2$. In case of a supercritical pressure difference, the instantaneous value of the mass flow through the critical hole should be determined by the expression [12]:

$$G = \frac{\mu F P}{\sqrt{RT}}\psi, \qquad (1)$$

where $\psi = \sqrt{k\left(\frac{2}{k+1}\right)^{\frac{k+1}{k-1}}}$; $\mu$ – mass flow range;

$F$ – injection area; k – adiabatic exponent of gas.

The current values of pressure and temperature in the bone in (1) are defined as [12]:

$$P = P_0\left(1 + Bt\cdot\right)^{\frac{-2k}{k-1}}, \qquad (2)$$

$$T = T_0\left(\frac{P}{P_0}\right)^{\frac{k-1}{k}}, \qquad (3)$$

where $B = \frac{(k-1)F\sqrt{RT_0}}{2V}\psi$; $V$ – volume of intermediate tank.

The ratio of the areas of the critical holes is established on the basis of the conditions at the initial instant of time $G_1/G_2 = \beta$, $P_1 = P_2 = P_0$, $T_1 = T_2 = T_0$. Then, from (1) we obtain:

$$F_1 = \beta \cdot F_2 \frac{\mu_2}{\mu_1}\frac{\sqrt{M_2}}{\sqrt{M_1}}\frac{\psi_2}{\psi_1}, \qquad (4)$$

where $M_1, M_2$ – molar masses of the gases forming the mixture.

We will proceed from the fact that in the course of the flow of gases from the tanks ensure the equality of the temperatures in them. Substituting for both components of expressions (2) and (4) into formula (3) for the current temperature, we obtain that relation $T_1 = T_2$ may be observed identically when the initial temperatures are equal $T_{10} = T_{20} = T_0$ and the ratio of the volumes of capacity, given by the expression

$$V_1 = \beta \cdot V_2 \frac{\mu_2}{\mu_1} \frac{M_2}{M_1} \frac{k_1 - 1}{k_2 - 1}. \quad (5)$$

In the case where the mixture forms gases with equal or close to the adiabatic exponents (for example, $N_2$+$O_2$, $N_2$+$H_2$, Ar+He and others.), provided that $P_{10} = P_{20} = P_0$ (4), and the volume of intermediate containers (5). On the basis of expression (1), the specified mass-consumption ratio is also automatically ensured without use of any regulating devices.

If it is necessary to form a mixture of gases with different adiabatic exponents ($CH_4$ + Ar, $Cl_2$ + $N_2$, $CH_4$ + $N_2$, etc.), when conditions (4) and (5) are fulfilled, the pressure in the gas tanks at the expiration will vary in different ways. However, if we abandon the requirement to ensure the consistency of the ratio of instantaneous mass expenditures of components, then it is possible to achieve the accuracy of providing a given mass concentration of gases in the mixture by setting the initial pressures in tanks, starting from the expression:

$$\frac{\int_0^\tau G_1 dt}{\int_0^\tau G_2 dt} = \beta, \quad (6)$$

where $\tau$ - time of filling the chamber with a mixture.

After substituting expressions (1) - (4) in (6), it is transformed to the form:

$$\frac{P_{01}}{P_{02}} = \frac{\int_0^\tau \left(1 + B_2 t\right)^{\frac{-2k_2}{k_2 - 1} - \frac{k_2 - 1}{2k_2}} dt}{\int_0^\tau \left(1 + B_1 t\right)^{\frac{-2k_1}{k_1 - 1} - \frac{k_1 - 1}{2k_1}} dt}. \quad (7)$$

The time of filling the working chamber with a mixture is determined by the achievement of a preset pressure level. The use of the equality condition for the enthalpies of the jets emanating from the high-pressure vessels and the jets that flow into the vacuum chamber leads to the following relationship between the pressure change in the vacuum chamber and the filling time [12]:

$$P_B = P_{01} \frac{V_1}{V_B} \left[1 - \left(1 + t \cdot B_1\right)^{\frac{-2k_1}{k_1 - 1}}\right] + P_{02} \frac{V_2}{V_B} \left[1 - \left(1 + t \cdot B_2\right)^{\frac{-2k_2}{k_2 - 1}}\right] + P_{B0}. \quad (8)$$

In expression (8), the first term stands for the partial pressure of the first component of the mixture, while the second one refers to the second component, and $P_{B0}$ stands for the residual pressure in the chamber after the process of evacuation. Then, assuming for definiteness that the correction of the initial pressure occurs in the capacity of the first component of the mixture to determine the value of $\tau$ from (8), we obtain:

$$\chi_2 \cdot P_P = P_{02} \frac{V_2}{V_B} \left[1 - \left(1 + \tau \cdot B_2\right)^{\frac{-2k_2}{k_2 - 1}}\right] \Rightarrow$$

$$\tau = \frac{\left(1 - \frac{\chi_2 \cdot P_P}{P_{02}} \frac{V_B}{V_2}\right)^{\frac{k_2 - 1}{-2k_2}} - 1}{B_2}, \quad (9)$$

where $P_P$ – the prescribed driving pressure in the chamber of the plasma unit; $\chi_2$ – the prescribed value of the mole fraction of the component in the mixture.

Let us consider the possibilities of ensuring the accuracy of dosing of the components of the mixture using the proposed method for the example of the $CH_4$-Ar mixture, which was considered as one of the variants in [2]. The following values are accepted as initial data for further calculations:

- $CH_4$: $\rho$ = 0.7168 [kg/m$^3$], M = 16.04·10$^{-3}$ [kg/Mole], k = 1.32, R = 518.37 [J/(kg·K)];
- Ar: $\rho$ = 1.7839 [kg/m$^3$], M = 39.948·10$^{-3}$ [kg/Mole], k = 1.67, R = 208.14 [kg/Mole)].

The volume of the vacuum chamber of the plasma installation was assumed equal to 500·10$^{-3}$ [m$^3$], the working pressure in the chamber was 100 [Pa]. The initial values of pressure and temperature in the tanks for methane and argon were taken equal to 0.5 [MPa] and 293 [K]. The values of the flow rates $\mu$ were taken equal to 1. The diameter of the critical hole for argon was chosen equal to $d_{Ar}$ = 0.1 [mm], and the volume of the intermediate capacity $V_{Ar}$ = 5·10$^{-3}$ [m$^3$].

The values of the diameter of the critical aperture and the volume of the intermediate capacity for methane calculated from the dependences (2) and (5) were rounded taking into account the manufacturing possibilities and amounted to $d_{CH4}$=0.249 [mm] and $V_{CH4}$=21.508·10$^{-3}$ [m$^3$]. The further calculations were specially made for the rounded-off values.

For the given values of the parameters, the time of filling the vacuum chamber to the preset pressure level was 5.231 seconds. Fig. 3 shows the graphs of the pressure change in the methane and argon tanks at an equal initial pressure. Because of the error caused by rounding the values of the critical hole diameter and the volume of the methane capacity, both pressure and temperature in the tanks vary in different ways. However, the difference in temperature in the bones during filling does not exceed 0.001 %. The correction of the initial pressure in the methane capacity allows us to accurately estimate the value of the ratio of the mass concentrations of the components (for the assumed bench-mark dat =3.6163462).

The Fig. 4 shows the graphs of the change in the instantaneous ratio of mass flow through the time of filling the vacuum chamber. Because of the errors assoc

iated with the rounding of the calculated values of the diameter of the critical hole and the capacity of methane, the initial dependence of the instantaneous mass flow ratio varies in time. In this case, the maximum deviation of the instantaneous value from the given value of β does not exceed 0.3 %, and the time-averaged filling ratio of the mass concentrations of the mixture components is 0.21 %.

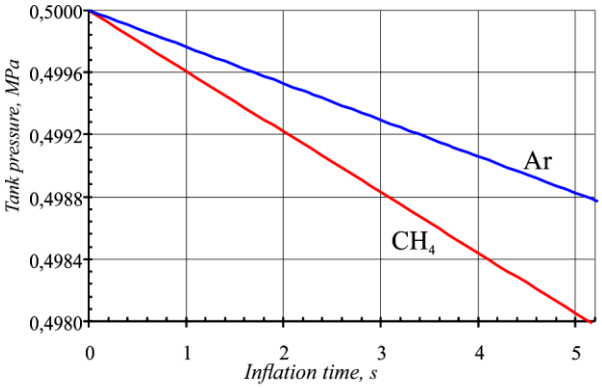


*Fig. 3. Dependences of pressure changes in methane and argon tanks at filling vacuum chamber*

The graph in Fig. 4 shows how the ratio of mass component costs changes after correction of the initial pressure in the methane methane batch using the dependence (7). We note that in this case the initial pressure value was also set taking into account the real pressure adjustment possibilities (up to 0.01 Bar). After such correction, the error of the time-averaged filling ratio of the mass concentrations of the mixture components from the set value was 0.01 %.

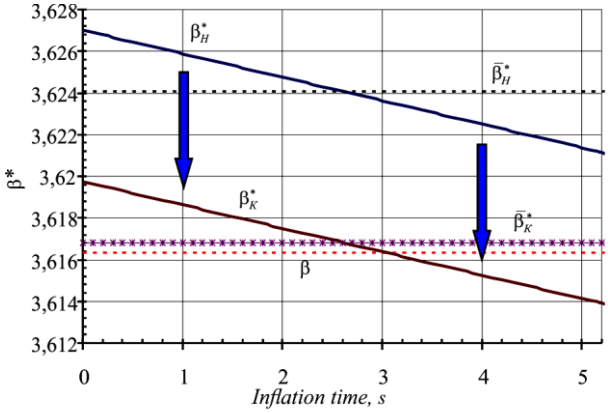


*Fig. 4. Dependences of the change in the mass flow ratio of the components of the mixture when the vacuum chamber is filled*

## CONCLUSIONS

1. This example confirms that the proposed method potentially significantly exceeds the basic version of the method of critical holes for the accuracy of dosing of gas mixture components. Its use requires high accuracy in the manufacture of individual parts and pressure adjustment. However, these settings are made before the process of generating the mixture begins. During the filling process, there are no devices that regulate the pressure or temperature, the presence of which is characteristic of the basic version of the method. This eliminates the inaccuracies associated with the measurement of parameters and the delays in the triggering of actuators.

2. The values of the flow rates μ entering in the dependences (4) and (5) for the areas of the critical holes and the volume of the intermediate tanks set the relationship between the theoretical and real flow through the gas mains and, strictly speaking, are not known at the beginning of the design calculations . The ratio of these coefficients can be determined, for example, in the course of a numerical simulation of the outflow of gases through critical holes. Another task of numerical modeling is the determination of the geometry of the mixer, which ensures homogeneity of the mixture during its mixing.

3. The accuracy of the proposed method can be improved by preliminary calibration. In the course of its implementation, the values of the flow rates in (4) and (5) must be specified. Another way to improve accuracy is to control the speed of opening the valves 9 and 19 (see Fig. 2), at which the ratio of the areas of their cross-sections defined by expression (4) is ensured at the time of opening and closing.

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## ДИНАМИЧЕСКИЙ МЕТОД СОЗДАНИЯ ГАЗОВЫХ СМЕСЕЙ ДЛЯ ПЛАЗМЕННЫХ ТЕХНОЛОГИЙ

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Рассмотрен вопрос создания многокомпонентных газовых смесей, предназначенных для использования в плазменных установках. Предложен динамический метод получения смесей газов, основанный на сверхкритическом истечении газов из ёмкостей через калиброванные отверстия. Показано, что при соответствующем выборе объёма ёмкостей и площадей критических отверстий может быть обеспечена высокая точность заданного состава смеси. В случае необходимости генерации газовой смеси из компонент, имеющих различные показатели адиабаты, предложено производить коррекцию начального давления газов в ёмкостях. Это также позволит компенсировать погрешности, связанные с изготовлением конструктивных элементов генератора смеси. Приведен пример расчета генератора смеси на основе предложенного метода, который подтверждает возможность обеспечения её компонентного состава с погрешностью порядка 0,01 %.

## ДИНАМІЧНИЙ МЕТОД СТВОРЕННЯ ГАЗОВИХ СУМІШЕЙ ДЛЯ ПЛАЗМОВИХ ТЕХНОЛОГІЙ

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Розглянуто питання створення багатокомпонентних газових сумішей, призначених для використання в плазмових установках. Запропоновано динамічний метод отримання сумішей газів, що базується на надкритичному витіканні газів з ємностей через калібровані отвори. Показано, що при відповідному виборі об'єму ємностей і площин критичних отворів може бути забезпечена висока точність заданого складу суміші. У разі необхідності генерації газової суміші з компонент, що мають різні показники адіабати і для компенсації похибок, пов'язаних з виготовленням конструктивних елементів генератора суміші, запропоновано проводити корекцію початкового тиску газів в ємностях. Наведено приклад розрахунку генератора суміші на основі запропонованого методу, який підтверджує можливість забезпечення її компонентного складу з похибкою близько 0,01 %.