Application of standard mixtures for the estimation of characteristics of non-equilibrium plasma of atmospheric pressure pulsed discharges

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Abstract. The non-equilibrium non-thermal plasma of atmospheric pressure (NNP), which is generated by electric discharges, is widely used in air-cleaning technologies. In this paper, it is proposed to use the method of standard mixtures to estimate the qualitative and quantitative parameters of the NNP. Pulsed corona discharge was used for the experiments. As testing mixtures, two groups of standard volatile organic compound mixtures with a certain qualitative and quantitative compositions were used. One of them contains a set of functional compounds used as solvents of wide application, and the other—a set of chlorine-containing compounds. Different components of the model mixture react with plasma components at different rates. Thus, by studying the concentration dependencies of such mixtures, one can obtain information about the qualitative and quantitative composition of the NNP generated by the chosen method and to determine the energy efficiency of the method.

1. Introduction
Electric discharges of various types are widely used to clean the air from vapors of volatile organic compounds (VOCs) [1]. Barrier discharge, streamer corona discharge, pulsed corona discharge, various types of glow discharges are intensively studied [2, 3]. The use of a non-equilibrium non-thermal atmospheric pressure plasma (NNP), created by the discharges, makes it possible to process air flow without significant thermal heating [4, 5]. However, air NNP treatment is accompanied by the release of toxic ozone [1]. Recently, effective combined technologies have been actively developed, in which the action of NNP is combined with the use of a catalyst [1,6–9]. The use of catalysts allows the decomposition of ozone, as well as the completion of oxidation of products of partial VOCs oxidation to harmless H₂O and CO₂. In order to investigate the mechanism it is necessary to study the individual stages of the processes, i.e. information that is lost when analyzing all processes in one pot. Therefore, researches using a single-stage VOC conversion procedure are also relevant and informative.

The mechanism of component removal and, consequently, the qualitative and quantitative composition of conversion products depends on both the NNP source and the chemical nature of removed impurities. Numerical simulation of elementary processes involved in the removal of VOCs from airflow is hindered by the absence of necessary kinetic constants. In addition, the variety of methods based on NNP of electric discharges and the variety of VOCs complicate the comparison of the efficiency of a given VOC removal by different methods under otherwise similar
conditions. To compare the efficiency of different methods, it was proposed to use the method of standard mixtures [10, 11]. All components of the model mixture are in equal conditions and participate in competing processes with plasma components. By constructing of a single common concentration dependencies, one can obtain information on the relative reactivity of each of the components. Taking into account the principle of reciprocity, we can say that these dependencies also carry information on the reactivity of the plasma, i.e. on the qualitative and quantitative composition of its active components. The composition of the components of the model mixture can be selected by the experimenter for a specific research task. In this paper it is shown that the method of model mixtures can also be used to estimate the parameters of NNP. Based on the experimental data presented in [11], it is shown that the method of standard mixtures can be used to estimate the qualitative and quantitative parameters of the NNP generated by pulsed corona discharge.

2. Experimental setup
The setup and conditions of the experiments were described in [10], the main concentration dependencies and analytical techniques are described in [11]. As a base part of the experimental setup, a high-voltage generator [12] was used, which formed in air a pulse of negative polarity with a current amplitude of 400 A; voltage pulse amplitude was 120 kV; voltage pulse full width at half maximum was 20 ns; pulse energy was 0.6 J and pulse repetition frequency was 10 Hz. In the case of a positive corona, the current amplitude was 300 A, and the pulse energy was 0.4 J.

The discharge chamber had an outer electrode in the form of the surface of a stainless steel tube with an internal diameter of 88 mm and a length of 56 cm. The chamber volume was 26 l. The parameters of the discharge was measured by an oscilloscope (Tektronix TDS–5054B) via appropriate matching circuits. To conduct the studies, a dry air of room temperature was used as the gas basis. The components of the mixture were added to the gas path in liquid state using a microsyringe.

Two model mixtures of various compositions were used. Mixture I included the widely used solvents: hexane (C6H14), benzene (C6H6), toluene (C6H5CH3), ethyl acetate (CH3COOC2H5), butyl acetate (CH3COOC4H9), acetone (CH3COCH3), and acetonitrile (CH3CN). As mixture II, chlorinated organic solvents of the following series were used: methylene chloride (CH2Cl2), chloroform (CHCl3), carbon tetrachloride (CCl4), dichloroethane (ClCH2CH2Cl).

The components of mixture I with a content of 0.1 ml each practically do not affect discharge parameters, whereas the addition of the same amount of the mixture II components leads to a decrease in the discharge current down to 200 A and a pulse energy to 0.35 J. The energy depositions into the gas (or specific energy), used as an independent parameter in the reducible concentration dependencies, were calculated from the oscillograms. The characteristic dependences of the change in the concentration of each component of mixture I from the specific energy E deposited in the gas in figure 1 at different polarities of the central electrode are presented.

In figure 2, the dependences for mixture II consisting of chlorine-containing components for different initial concentrations are presented.

3. Results and discussion
Concentration dependencies were analyzed by the methods of formal kinetics [13–16]. The fundamentals of the improved method in the application to multicomponent mixtures are presented in [11]. For a simplified description of the processes, it is possible to represent the set of active plasma components by one some formal reagent R. The process of removing the component of mixture X_i is written down by the equation
\[
\frac{dX_i}{dE} = -k_i[R][X_i].
\]
Figure 1. Component concentrations $X_i$ as functions of specific energy $E$, deposited in gas by discharge for mixture I with initial concentrations of 1000 ppm each: 1—acetonitrile; 2—acetone; 3—ethyl acetate; 4—benzene; 5—butyl acetate; 6—hexane; 7—toluene for negative corona discharge (a) and positive corona discharge (b).

Figure 2. Component concentrations $X_i$ as functions of energy $E$, deposited in gas by discharge for mixture II: 1—CH$_2$Cl$_2$; 2—CHCl$_3$; 3—CCl$_4$; 4—ClCH$_2$CH$_2$Cl. Initial concentrations of components 1 to 4: 1400, 1050, 970, 1200 ppm, respectively (a); 190, 150, 130, 160 ppm, respectively (b).

Generation and destruction of the formal reagent $R$ is described by the equation

$$
\frac{dR}{dE} = K_g[R] - K_d[R] - \sum_{i=1}^{N} k_i[R][X_i],
$$

where $N$ is a number of mixture components.
Under quasi-stationary conditions, the expression of approximation can be used as

\[ K_g - K_d - \sum_{i=1}^{N} k_i[X_i] = 0. \]  

(3)

A rough estimate of the relative reactivity of each component can be performed graphically, starting from the experimental concentration dependencies shown in figures 1 and 2. Using the initial part of the concentration curve, we can estimate \( \Delta[X_i]/\Delta E \approx -k_i[R][X_i] \). Taking into account that all components \( X_i \) are in equal conditions, for equal values of \( R \), the constants \( k_i \) will be related to each other approximately as \( \Delta[X_i]/(\Delta E([X_i] + \Delta[X_i]/2)) \). Using the data after entering the energy \( \Delta E = 140 \text{ J/l} \) into the gas, assuming that \( \Delta[X_i] = [X_i]_0 - [X_i] \), where \( [X_i]_0 \) is initial admixture concentration \( X_i \), we can determine the current values of \([X_i] \) and \( \Delta[X_i] \) and calculate the necessary expression for each component of the mixture.

Establishing the reactivity of one of the component as a standard, the relative reactivity of remaining components may be calculated from it. The study of a large number of publications on the conversion of VOCs under the action of NNP has shown that in studies the most often used VOC is toluene; the removal tasks are most relevant, see for example [1, 17, 18]. Toluene can be taken as a standard of reactivity and we may calculate the relative reactivity of all other used VOC is toluene: the removal tasks are most relevant, see for example [1, 17, 18]. Toluene on the conversion of VOCs under the action of NNP has shown that in studies the most often remaining components may be calculated from it. The study of a large number of publications in the case of mixtures is used to remove all components at once and to different degrees, \( R \). As one can see from these values, if the positive polarity of the pulse is used, the relative reactivity of the components differs little from that for a discharge with a negative polarity of the corona. At the same time, the energy expenditure for removing each component is proportionally decreases as shown in figure 1(b). In the literature, a different effects of the polarity of the corona are in equal conditions, for equal values of \( R \).

As one can see from these values, if the positive polarity of the pulse is used, the relative reactivity of the components differs little from that for a discharge with a negative polarity of the corona. At the same time, the energy expenditure for removing each component is proportionally decreases as shown in figure 1(b). In the literature, a different effects of the polarity of the corona on the process are described, for example, in the case of removal of styrene [19, 20].

Model mixtures can also be used to calculate the energetic parameters of the components deletion. Expression \( dX_i/dE \) in this form in the recalculation of dimensions is none other than the plasma-chemical yield of the removal process \( G_i, \text{ molecule/heV} \), which is directly related to the energy cost of removing one molecule \( \varepsilon, \text{ eV/molecule} \): \( \varepsilon = 100/G_i \). The value of the plasma-chemical yield of the \( i \)-th component \( G_i \) is directly proportional to the described above relative constants \( k_i \) or \( k_{i, \text{toluene}} \). Using the energy input 140 J/l from the data shown in figure 1(a), it is possible to calculate \( G_i \) = 0.7 (toluene), 0.70 (hexane), 0.54 (butyl acetate), 0.32 (benzene), 0.24 (ethyl acetate), 0.16 (acetone) and 0.08 molecule/heV (acetonitrile). Obviously, the reagent \( R \) in the case of mixtures is used to remove all components at once and to different degrees, therefore, taking into account (3), it may be concluded that for a sufficiently large concentration of all components, the deactivation term becomes relatively small, what allows to record

\[ K_g[R] \approx \sum_{i=1}^{N} k_i[R][X_i], \]  

then

\[ G_g \approx \sum_{i=1}^{N} G_i, \]  

where \( G_g \) is the generalized energy yield of removing the mixture of \( N \) components. For the dependency conditions shown in figure 1(a), \( G_g = 2.74 \text{ molecule/heV} \). This value depends on the initial concentration of the components, as shown in figure 3. At high component concentrations,
Figure 3. The total yield $G_g$ as a function of the initial concentration $X_0$ of all components (acetonitrile, acetone, ethyl acetate, benzene, butyl acetate, hexane, toluene).

$G_g$ tends to a certain value that is numerically equal to the energy yield of the pseudoreagent $R$, demonstrated in figure 3 as $G_R$.

Similar estimates were given for mixture II, according to the dependence conditions shown in figure 2. The calculation shows the values of the yields $G_i = 0.15$ (CCl$_4$), $0.25$ (CHCl$_3$), $0.35$ (CH$_2$Cl$_2$) and $0.62$ molecule/heV (ClCH$_2$CH$_2$Cl). The total yield $G_g = 1.37$ molecule/heV. Its dependence obtained for low concentrations shown in figure 2(b), but it indicates that the nature of the concentration dependencies changes significantly with a decrease in concentration of components, as can be seen from the data of the dependencies for ClCH$_2$CH$_2$Cl. It indicates the prevalence of one mechanism over another under the selected conditions. For example, this can be explained by the significant contribution of the processes of electron dissociative attachment for chlorohydrocarbon molecules in the case of low concentrations. For similar processes, see [21].

A significant effect of the similar electron attachment processes was noted in [22]. In this case, the relative reactivity of the components changes significantly with a change in concentration, which indicates that the assumption of some single pseudoreagent R is not applicable, it is necessary to consider several reagents $R_j$, therefore (1) should be considered as

$$\frac{dX}{dE} = -k_i \sum_{j=1}^{M} [R_j][X_i],$$

where $M$ is the number of groups of plasma components that determine the process of conversion of the components of a model mixture. This consideration allows us to estimate the number of major groups of processes involved in the removal of impurities. The use of model mixtures with components of different nature will make it possible to distinguish the groups of the main active components of the plasma when the composition of the gas mixture changes (the content of oxygen, water vapor, etc) and the influence of the parameters of the electrophysical method on their yield. Thus, the method of model mixtures makes it possible to evaluate the qualitative and quantitative composition of a non-equilibrium plasma, however, in order to increase its informativity, it is necessary to select the components of model mixtures for a particular problem. The search for such mixtures is the creative task of future research.
4. Conclusion
The method of standard mixtures allows evaluating the qualitative characteristics as well as and quantitative ones for the components of a non-equilibrium plasma of a pulsed corona discharge. These conclusions can also be used to characterize other methods of generating NNP and to compare them. The question of the optimal composition of the model mixtures remains open.

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