Model compound mixtures for studying the main trends of volatile organic compounds conversion in processes of air cleaning by pulsed discharges

I E Filatov, V V Uvarin and D L Kuznetsov
Institute of Electrophysics UD RAS, 106 Amundsen Str., Yekaterinburg, 620016, Russia
E-mail: fil@iep.uran.ru

Abstract. To study the process of removing volatile organic compounds (VOCs) vapors from air flow by the action of pulsed discharge plasma, it is proposed to use specially selected model mixtures of components. The components of these mixtures are in equal conditions, which makes it possible to measure the relative reactivity with high accuracy without using high-speed analysis techniques. Using three groups of the mixtures, it was shown that substances with different functional groups react with different components of the discharge plasma. Multifunctional VOCs react with active forms of nitrogen and oxygen. Halogenated compounds are mainly removed due to electron attachment processes, and unsaturated compounds are removed by reaction with ozone.

1. Introduction
Volatile organic compounds (VOCs) are part of the air emissions of many industrial enterprises [1]. They are distinguished by a wide variety of physical and chemical properties and toxic effects on humans and the environment. A number of promising technologies for the purification of air from VOC vapor is based on the processing of polluted air flows with electric discharges of various types, including in combination with catalytic methods [2–9]. The study of the behavior of VOCs in a non-equilibrium plasma of the discharges is associated with a number of specific difficulties. The absence of data on the rate constants of the lot of VOCs reactions with plasma components complicates mathematical modeling. Experimental data are obtained in different conditions, the uniformity of concentrations and temperature is difficult to ensure. As a result, the data obtained at different portable experimental installations by different experimenters are difficult to compare. And the process itself is difficult to scale. Some researchers offer some interesting formal models for scaling processes, for example [10]. However, these models also have disadvantages, for example, with reproducible measurement of energy parameters, correct and reproducible chemical analysis. A universal and accurate method for analyzing the chemical composition is the method of gas chromatography (GC), which, however, requires a long measurement time (from several to tens of minutes), reflects only a certain stationary equilibrium intermediate composition, and information on the speed of processes is lost when it is used.

Earlier, we proposed an experimental technique based on the use of special model mixtures for research [11–13]. The essence of this technique is that the components of mixtures are investigated in equal experimental conditions, so it makes it possible to compare their reactivity correctly and to carry
out other relative measurements with high accuracy. If one of the components has a set of known properties (used as a standard), then the reaction parameters of the other components can be estimated against it. Fast plasma-chemical processes occur with many components simultaneously and under equal conditions and are completed by the time a slow analytical method such as GC is implemented. Therefore, the distribution of the concentrations of the components of the mixture is like a "photo" of fast processes. The selection of the composition of such mixtures is a creative and interesting task. To obtain more accurate results, it is important that the components of the mixture have a comparable reactivity (within the same order of magnitude) with respect to the components of the plasma. Then for the study, you can use the so-called method of competing reactions. It is also desirable that the components are removed from the air by similar mechanisms. Considering this, we selected separate groups of the studied mixtures. For studies of plasma conversion, based on our own experience and literature, we can distinguish groups of compounds with different chemical properties with respect to the components of the plasma and their derivatives:

- **Moderately reactive functional compounds.** These compounds interact with plasma components at a moderate rate. The reaction components are active oxygen and nitrogen forms, water decomposition products: atomic hydrogen, hydroxyl radical;
- **Halogenated compounds.** It is interesting that the electron attachment processes play an important role in their removal.
- **Unsaturated compounds.** Compounds with increased reactivity with respect to ozone.

Obviously, this list is not exhaustive and may be expanded, depending on the specific research tasks.

The studies were carried out using a nanosecond pulsed corona discharge as a source of non-equilibrium plasma. Such discharges create high concentrations of active particles as the initiators of plasma-chemical reactions, and their parameters do not depend so much on the design of the discharge chamber and the gaseous medium (as is typical of dc discharges and barrier discharges).

2. Experimental setup

In the experiments, the installation [12] was used based on the generator SM-4N [14]. The discharge parameters were as follows: voltage pulse amplitude – 120 kV, duration – 20 ns, current amplitude – 300 A. The pulse energy was calculated from the waveforms \( U(t) \) and \( I(t) \) for each pulse series using the formula: \( E_p = \int U(t)I(t)\,dt \). The air mixture was processed by a series of pulses with a frequency \( f = 10 \) Hz and a duration \( t = 1 \) min, followed by a pause with a duration of \( 4 \) min, which is necessary for performing GC analysis using a flame ionization detector. The specific energy \( E \) was calculated for a series of pulses using the formula: \( E = E_p f \tau / V \), where \( V \) is the volume of the gas system, \( V = 26 \) l. The content of O\(_3\) was estimated by absorption at a wavelength of 255 nm using a «Specord-200» spectrophotometer with a gas cell of 1 cm thick using absorption tables [15]. The gas system of the plasma-chemical reactor was able to mix gaseous components in a closed cycle using an integrated fan. This ensured high reproducibility of analytical results: the error in measuring the concentration of components did not exceed 3–5%.

3. Results and discussion

The main components of air are oxygen and nitrogen. Under the action of a non-equilibrium pulsed discharge plasma, the formation of active forms of nitrogen and oxygen occurs. However, molecular oxygen, although a source of active ingredients, also neutralizes them. For example, atomic oxygen, although it effectively reacts with many VOCs, is intercepted by molecular oxygen, which is in great excess. As a result, ozone is always produced. Ozone reactivity is not enough to remove the vast majority of VOCs quickly. Ozone is a highly toxic component, so treatment plants must ensure its decomposition. Catalysts [5, 9] are commonly used for this. However, to understand the processes in our opinion, it is necessary to investigate the stage before ozone decomposition separately and specifically. The ozone content is an important characteristic in the study of plasma-chemical processes in the air, because its formation can be considered both side and the main process of air
purification. Despite the fact that the real problems of cleaning gas streams from VOC impurities in the overwhelming majority of cases mean the oxygen content of about 20%, the study of processes in gas streams under conditions with low oxygen content and even nitrogen is of great importance, since reveal the role of oxygen in the process (passivating or activating). Therefore, experiments in air mixtures, and in nitrogen, were conducted in studies.

3.1. Moderately reactive functional compounds
A mixture of compounds was used for the study: hexane (C₆H₁₄), benzene (C₆H₆), toluene (C₆H₅CH₃), ethyl acetate (CH₃COOC₂H₅), butyl acetate (CH₃COOC₄H₉), and acetone (CH₃COCH₃). The mixture is similar to that used in [12]. These compounds are widely used as solvents for paints and varnishes. Earlier it was shown that the use of such a mixture allows us to calculate the relative reactivity of each of the components with respect to the plasma components [12]. Here is a portion of the similar studies in air mixture with measurements of ozone concentration and in pure nitrogen for comparison. For convenience of comparison, equal concentrations of all components were used – 250 ppm each. Figure 1 shows the concentration dependences of the components designated as \( X_i \) on the characteristic energy \( E \) with an equal concentration of all components – 250 ppm each: a: in dry air, b: in dry nitrogen. Figure 1a also shows the concentration dependence of ozone and, for comparison, shows that for clean air. In the presence of impurities, ozone production is slowed down, which indicates that the formation of ozone is a competing process in relation to the process of removing impurities. From the slopes of the dependences 7 and 6 of figure 1a, one can calculate the plasma-chemical ozone yield, which is 3.7 molecules/100 eV in the case of clean air and 2.6 molecules/100 eV in air with impurities.

![Figure 1](image)

**Figure 1.** Dependences of the concentrations of components of the mixture \([X_i]\), ppm and ozone \([O_3]\), ppm on the specific energy deposition \(E\), J/l for dry air (a) and nitrogen (b), respectively. The numbers indicate the dependencies: 1 – CH₃COCH₃, 2 – C₆H₆, 3 – CH₃COOC₂H₅, 4 – CH₃COOC₄H₉, 5 – C₆H₁₄, 6 – C₆H₅CH₃. Ozone concentration: 7 – for air without impurities and 8 – for air with \( X_i \) components.

In figure 1b for comparison, the results of processing the mixture of components in dry nitrogen are presented. It is known, that unsaturated compounds have increased reactivity with respect to ozone [16–18]. Thus, figure 2 shows the results of the experiment, similar to the conditions of figure 1a with the addition of 500 ppm styrene.

It is clear that the formation of ozone occurs only after complete removal of styrene. Using the experimental data presented in figures 1 and 2, the relative reactivities of each of the components relatively to toluene were calculated according to the procedure described in [12]. The coefficients of reactivity relatively to toluene \( k_i, \text{toluene} \) are shown in table 1.
Figure 2. Dependences of the concentrations of components of the mixture \([X_i]\), ppm and ozone \([O_3]\), ppm on the specific energy deposition \(E, J/l\) in dry air. The numbers indicate the dependencies: 1 – CH₃COCH₃, 2 – C₆H₆, 3 – CH₃COOC₂H₅, 4 – CH₃COOC₄H₉, 5 – C₆H₁₄, 6 – C₆H₃CH₃, 7 – C₆H₅CH=CH₂, 8 – ozone concentration \([O_3]\), ppm.

Table 1. The dependences of \(k_{i, \text{toluene}}\) for a mixture of components in different conditions.

| Component   | Conditions | air  | N₂   | Air + C₆H₅CH=CH₂ |
|-------------|------------|------|------|------------------|
| CH₃COCH₃    |            | 0.17 | 0.52 | ~ 0.11           |
| C₆H₆        |            | 0.32 | 0.67 | ~ 0.11           |
| CH₃COOC₂H₅ |            | 0.37 | 0.56 | ~ 0.11           |
| CH₃COOC₄H₉ |            | 0.80 | 0.81 | ~ 0.31           |
| C₆H₁₄       |            | 0.95 | 0.71 | ~ 0.31           |
| C₆H₅CH₃    |            | ≡ 1.00 | 1.08 | ~ 0.31           |
| C₆H₅CH=CH₂ |            |      |      | 5.23             |

\(^a\) the concentration of all components \([X_i]\) = 250 ppm, except C₆H₅CH=CH₂, for which \([X_{\text{styrene}}]\) = 500 ppm

Interestingly, in pure nitrogen, the energy efficiency of some impurities decreases slightly, and the removal efficiency of acetone, ethyl acetate and benzene even increases, indicating a significant contribution of active nitrogen forms to the process of removing multi-functional compounds. The activity of styrene in air is more than 5 times higher than that, due to its increased reactivity with respect to ozone. In order to clarify more subtle mechanisms, the solution of inverse kinetic problems is required. This is planned to be done in the near future.

3.2. Halogenated compounds

The mechanism for the removal of halogen-containing VOCs differs from that for the above because of the significant contribution of electron attachment processes \([2]\). Indeed, even the presence of these compounds in air at a concentration of about 0.1%, reduces the discharge current by 20–30% and the pulse energy by about the same amount. A mixture of compounds: carbon tetrachloride (CCl₄), chloroform (CHCl₃), methylene chloride (CH₂Cl₂) and dichloroethane (CICH₂CH₂Cl) was used for the study. The mixture is similar to the one used previously \([12, 13]\). These solvents are widely used for degreasing and dissolving plastics. Here are comparative studies of the mixture in dry air (with ozone concentration measurement) and nitrogen. The results are shown in figure 3. From the slopes of curves 5 and 6 from figure 3a, one can calculate the plasma-chemical ozone yield, which is \(G_{O_3} = 3.4\) molecules/100 eV in the case of clean air and \(G_{O_3} = 2.4\) molecules/100 eV in air with impurities. In nitrogen, as shown in figure 3b, the chlorinated components are removed more efficiently. This can be explained by the fact that the oxygen of the air intercepts a significant part of
the electrons involved in dissociative attachment, as an important process leading to a decrease in the concentration of impurities. The relative reactivity of the components can be calculated relatively to dichloroethane (DCE) and is designated as \( k_i, \text{DCE} \).

DCE is convenient to use as a standard in our case, since the change in its concentration during the measurement process significantly exceeds the experimental error and therefore can be used as a reliable value. The coefficients of the relative reactivity with respect to DCE \( k_i, \text{DCE} \) are shown in Table 2.

![Figure 3](image)

**Figure 3.** Dependences of the concentrations of the components of the mixture \([X_i]\), ppm and ozone \([O_3]\), ppm on the specific energy deposition \( E, \text{J/l} \): (a) for dry air and nitrogen, respectively. The numbers indicate the dependencies: 1 – CCl\(_4\), 2 – CH\(_2\)Cl\(_2\), 3 – CHCl\(_3\), 4 – ClCH\(_2\)CH\(_2\)Cl. Ozone concentration: 6 – for air without impurities and 7 – for air with \( X_i \) components.

### Table 2. The dependences of \( k_i, \text{DCE} \) for a mixture of components in different conditions.

| Component \( X_i \) | \( k_i, \text{DCE} \) \( \text{air} \) | \( k_i, \text{DCE} \) \( \text{N}_2 \) |
|---------------------|------------------|------------------|
| CCl\(_4\)           | \( \sim 0.50 \)  | 1.11             |
| CH\(_2\)Cl\(_2\)    | \( \sim 0.50 \)  | 1.90             |
| CHCl\(_3\)          | \( \sim 0.50 \)  | 2.29             |
| ClCH\(_2\)CH\(_2\)Cl| 1.00             | 4.47             |

The relative reactivity of chlorine-containing compounds to active plasma particles largely depends on the concentration. Therefore, the data presented here is different from [12]. The apparent violation of the law of mass action is due to the presence of additional unrecorded mechanisms for removing compounds. In order to clarify more subtle mechanisms, the solution of inverse kinetic problems is required. This is planned to be done in the near future.

### 3.3. Unsaturated compounds

Unsaturated compounds are widely used as monomers in the plastics industry. The double bond provides an increased reactivity of such compounds with respect to ozone [16–18]. Unsaturated compounds, styrene and methyl methacrylate (MMA) were chosen as objects of study. Figure 4 shows the results of experiments in air (a) and nitrogen (b). The measurement of ozone concentration (curve 3) shows that the ozone production begins only after the impurities are removed and reaches the value \( G_{O3} = 3.97 \text{ molecules/100 eV} \). In nitrogen, impurities are removed less efficiently. Such a
character of dependences suggests that the main mechanism for the removal of unsaturated compounds is their reaction with ozone.

![Figure 4](image.png)

**Figure 4.** Dependences of the concentrations of the components of the mixture $[X_i]$, ppm and ozone $[O_3]$, ppm on the specific energy deposition $E$, J·l$^{-1}$ for dry air (a) and nitrogen (b), respectively. The numbers indicate the dependencies: 1 – MMA, 2 – styrene, 3– ozone concentration for air with $X_i$ components.

The construction of concentration dependences with a large change in concentrations allowed us to solve the inverse kinetic problem – the solution is shown in the form of solid lines. The ratio of the reaction constants found for styrene ($k_1$) and MMA ($k_2$) agrees well with the ratio of the rate constants for the interaction of styrene ($k_{St}$) and MMA ($k_{MMA}$) with ozone: $k_{St} = 1.5 \times 10^{-17} \text{ cm}^3 \cdot \text{s}^{-1}$ [18], $k_{MMA} = 6.7 \times 10^{-18} \text{ cm}^3 \cdot \text{s}^{-1}$ [17]. At the same time, $k_{MMA}/k_{St} = 0.45$, which is very close to the value of $k_2/k_1 = 0.44$. Curves 1 and 2 of figure 4a are well described by solving the direct kinetic problem using only the processes of interaction of unsaturated compounds with ozone for calculations. Thus, it has been shown that ozone is the main active agent in the removal of unsaturated compounds using a pulsed discharge in air. In this case, the capabilities of the competing reaction method are demonstrated, which makes it possible to estimate the reactivity of VOCs with respect to plasma components with high accuracy if the compound is used in a mixture with another compound, the parameters for which are known.

4. Conclusion

The possibilities of the standard mixture method for the study of air purification processes from different classes of VOCs are demonstrated. It is clearly shown that molecular oxygen in some cases takes part in the deactivation of the active components of non-equilibrium plasma of pulsed discharges (electrons and atomic oxygen). The reactivity of the resulting ozone is only enough to clean the air from the vapors of unsaturated compounds. The method of standard mixtures used allows one to obtain a greater amount of information for a single experiment, which makes it possible to increase significantly the efficiency of research on the development of promising air purification technologies using a non-equilibrium discharge plasma.

Acknowledgments

The work was supported by the Russian Foundation for Basic Research (grant No. 17-08-01212).

References

[1] Schnelle Jr K B, Dunn R F and Ternes M E 2015 *Air Pollution Control Technology Handbook* (Boca Raton – London – New York – Washington, D.C.: CRC press)
[2] Vandenbroucke A M, Morent R, De Geyter N and Leys C 2011 J. Hazard. Mater. 195 30
[3] Schmidt M, Jogi I, Holub M and Brandenburg R 2015 Int. J. Environ. Sci. Technol. 12 3745
[4] Xiao G, Xu P, Wu R, Ni M, Du C, Gao X, Luo Z and Cen K 2014 Plasma Chem. Plasma Process. 34 1033
[5] Liang C J and Fang J W 2016 Chem. Eng. Sci. 144 101
[6] Ojala S et al 2011 Top. Catal. 54 1224
[7] Chen H L, Chang M B, Lee H M, Chen S H, Yu S J and Li S N 2009 J. Environ. Sci. Technol. 43 2216
[8] Van Durme J, Dewulf J, Leys C and Van Langenhove H 2008 Appl. Catal. B 78 324
[9] Kim H H, Ogata A and Futamura S 2006 IEEE Trans. Plasma Sci. 34 984
[10] Parvulescu V I, Magureanu M and Lukes P 2012 Plasma Chemistry and Catalysis in Gases and Liquids (Weinheim: Wiley, VCH Verlag & Co. KGaA)
[11] Filatov I E, Uvarin V V and Kuznetsov D L 2016 Tech. Phys. Lett. 42 927
[12] Filatov I E, Uvarin V V and Kuznetsov D L 2018 Tech. Phys. 63 680
[13] Filatov I E, Uvarin V V and Kuznetsov D L 2019 J. Phys.: Conf. Ser. 1147 012122
[14] Rukin S N 1999 Instrum. Exp. Tech. 42 439
[15] Molina L T and Molina M J 1986 J. Geophys. Res.: Atm. 91 14501
[16] Poznyak T I, Oria I C and Poznyak A S 2019 Ozonation and Biodegradation in Environmental Engineering (Amsterdam – Oxford – Cambridge: Elsevier) p 325
[17] Le Person A, Eyglunent G, Daële V, Mellouki A and Mu Y 2008 J. Photochem. Photobiol. 195 54
[18] Bernard F, Eyglunent G, Daele V and Mellouki A 2010 J. Phys. Chem. A. 114 8376