

Effect of Ionizing Radiation on the Formation of Nanoparticles in the Atmosphere

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Abstract

The resources of real atmosphere at the size reference areas in polar, mountainous, arid and other regions are evaluated experimentally from the viewpoint of ion-stimulated synthesis of aerosol particles. Air, from which the dust was preliminarily removed, was ionized with the radiation of plutonium 239 isotope with the ionization current equal to 1 μA . With the physical upper limit of the yield of condensed radiolysis products equal to 25–40 molecules per 100 eV of absorbed radiation, the achieved level is 5–10 molecules /100 eV, depending on irradiation time and on the state of the surface air layer.

INTRODUCTION

The formation of stable aerosol particles in ionized air was observed with a number of organic gases added to air, in particular acetylene, benzene [1]. For the concentration of these impurities $M_g = (10^{-1}-1)$ ppm, aerosol yield is $M_a = 10 \text{ mg/m}^3$. However, at the concentrations within (10^2-10^3) ppm saturation occurred: $M_a = 40-50 \text{ mg/m}^3$.

During the years 1960–1990, researchers started to report on the formation of the particles of nonvolatile condensate (so-called “radiolytic aerosol” (RA)) under ionization of the air purified from foreign gaseous and aerosol impurities. Such facts were observed in the experiments involving α -emitting isotopes of toron-220 [2, 3], actinon-214 [4], polonium-210 [5, 6], radon [7] and plutonium-239 [3, 8], β -emitting isotopes of thallium-204 [9] and strontium-90 [10, 11], X-ray radiation with the energy of 250 keV [9], electron beams [12], UV radiation [13, 14], etc. [1].

Gradually, an opinion was formed (for example, see [15–18]) that the ion-stimulated mechanism of aerosol generation is geophysically significant, in particular, for more complete account of the consequences of nuclear catastrophes. For instance, according to the data of [8], with the energy contribution from ionizing radiation into the surface air layer of the order of $10^{11}-10^{12} \text{ eV/cm}^3$, which is characteristic of the Chernobyl APP disaster zone, the concentration of radiolytic aerosol in the ionization zone can reach the values comparable with, or exceeding, the level of aerosol pollution in smog.

The goal of the present work was experimental evaluation of the resources of surface air layer as a source of aerosol particles more than 5 nm in diameter under ionization with radioactive radiation. Since a substantial contribution into natural ionization of the air is made by isotopes (radon, toron, etc.) emitting alpha particles with the energy about 5–7 MeV, ionizer based on plutonium-239 nuclide (with the mean energy of 5.4 MeV) was used in the experiments.

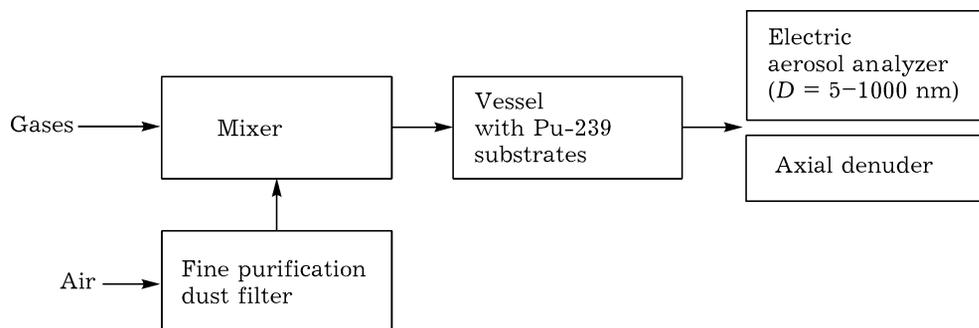


Fig. 1. Simplified scheme of the experimental unit for intensive ionization of the air.

INSTRUMENTATION AND PROCEDURES

Measurements were carried out under the conditions of forest-steppe (Ukraine, the region of Chernobyl APP, June 1986 and 1987), high-mountain region (Pamir, 3000 m, September 1989), sandy desert (southern Tajikistan, Shaartuz settlement, September 1989), near-polar sea (Kola Bay, December 1989), deciduous forest and a small town (100 km south-west from Moscow, Obninsk, March–June, 1986). The experimental procedure involved measurement of the concentration, particle size and chemical composition of aerosol formed at the outlet of a flow ionizer. Outdoor air purified preliminarily from dust was supplied to the inlet of the ionizer.

The ionizer (Fig. 1) is a cylindrical box with the cross section of 40 cm² and 10 cm long. Six plates of Pu-239 isotope, with the total activity of 400 μ Cu, were placed at the walls of the box. Ionization current strength (I) under normal atmospheric conditions was (1 ± 0.25) μ A. The intensity of ion formation $q_i = I/(Be)$ averaged over the box volume $B = 400$ cm³ did not exceed $1.5 \cdot 10^{10}$ cm⁻³s⁻¹, where e is ion charge equal to $1.6 \cdot 10^{-19}$ C. Atmospheric air and reference gases entered a mixing unit and then passed into the ionizer after fine purification from the background aerosol particles. Measurement of particle size was carried out with the help of an electric aerosol analyzer, model 3030, of Thermosystems Inc., USA.

Air flow through the ionizer was equal to aerosol flow through the electric analyzer, so the minimal irradiation time was about 5 s. An increase in irradiation time to 1000 s was achieved by pausing with air admission to the

chamber for a definite time interval. Then the pump was switched on, and the signal of ion current for the given voltage at the mobility separator of the analyzer was recorded for several seconds. Measurements were repeated with stepwise changes in the separator potential from 20 to 11 000 V over the number of aerosol size scales (11 scales in our experiments).

Air and aerosol were also sampled at the outlet of the ionizer into a gas axial denuder for subsequent analysis by means of high-performance liquid chromatography.

MAIN IONIZATION PRODUCTS

Rather intensive bipolar ionization of usual air is known to result in changes in the ion, aerosol and gas composition of the air. In turn, the state of air affects the yield of radiolysis products [1]. So, in order to solve the formulated problem, it is necessary to know variability of the yield of these products as a function of meteorological and other local factors. As the initial data, we will consider the results of measurements carried out with the help of the ionizer under the conditions of a forest land near Obninsk.

A diagram shown in Fig. 2 illustrates the state of gaseous products (ozone, nitrogen oxide and dioxide), ionic species (light- and medium-weighted ions) and aerosol formed under irradiation for about 6 s in the samples of the outdoor air. For comparison, the data on the same components averaged for non-perturbed surface air layer (that is, under natural ionization) are also shown. The calculated data for neutral ion clusters will be discussed below.

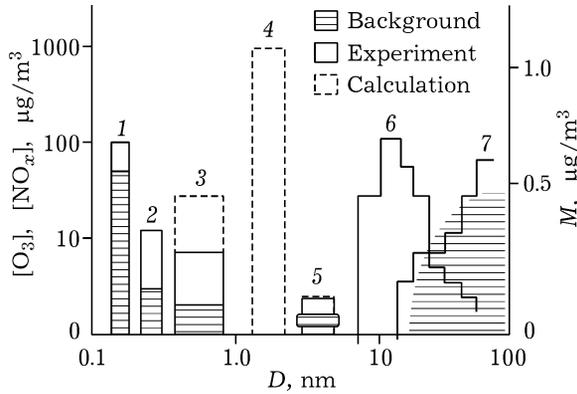


Fig. 2. Comparison of the mass concentrations of gases, ions (M_{\pm}), neutral clusters ($M_{n.c}$) and aerosol (M_a) before and after intensive ionization of the air with the radiation of Pu-239 isotope (activity: 400 μ Cu, ionization current strength: 1 μ A; air temperature: (21 ± 2) °C, relative humidity: (60 ± 10) %, pressure: (950 ± 30) gPa): 1 - O_3 , 2 - NO_x , 3, 5 - light and middle ions, respectively, 4 - clusters, 6, 7 - new and background aerosol, respectively; calculated $M_{n.c}$ and M_{\pm} values were obtained using equations (1) and (2).

According to the notions available (for example, see [15, 19, 20], the initial products of air ionization are molecular ions (N_2^+ , O_2^+ , NO_x^+ , CO_2^+ , H_3O^+), as well as some gases (O , N , O_3 , NO_x , etc.). Due to hydration, light-weighted ions containing 3–5 water molecules are formed within the time equal to or less than a millisecond. The prevailing character of the formed bonds is ion dipole, their length is about three times as large as the size of water molecule or another ligand. With the lifetime of a light-weighted ion equal to 1 s or more, the position of the central nucleus is occupied by the molecules of stronger electronegative gases and vapours (in particular, nitrogen oxides, halo-gens, etc.) and proton acceptor gases (water vapour, some acids).

In the case of rather intensive ionization, ion-molecular reactions also result in the formation of nitrogen oxides N_2O , NO_2 , NO and HNO_3 molecules. For irradiation time ~ 1 s, ion complexes $NO_3^-(H_2O)_n$, $NO_3^-HNO_3 \cdot H_2O$, $H_3O^+(H_2O)_m$, etc. appear in the atmosphere [20]. The mobility u_{\pm} of these ions is within the range $1-3$ $cm^2/(V \cdot s)$; the modes of negative and positive light-weighted ions are well resolved with the spectrometer: $u_+ \sim 1.3$ $cm^2/(V \cdot s)$, $u_- \sim 1.6$ $cm^2/(V \cdot s)$.

Following [1, 15] we will assume that a collision of differently charged light-weighted ions results in the formation of a stable neutral

complex or an ion pair with the diameter about twice as large as the diameter of the light-weighted ion ($D_n \approx 1.5-2$ nm) and the mass equal to that of 10–15 water molecules. The complex has a structure of the dissociated nitrous oxide molecule [$NO_3^-(H_2O)_n + H_3O^+(H_2O)_m$] or [$NO_3^-(HNO_3)_n + H_3O^+(H_2O)_m$]. Since the character of bonding in the complex is combined (Coulomb plus hydrogen-type), the complex exhibits all the properties of a physical cluster, first of all stability.

A characteristic time of the formation of neutral clusters $\tau_{n.c}$ can be estimated neglecting other sinks of light-weighted ions: $\tau_{n.c} \approx (q_i \gamma_{n.c})^{-1/2} = 0.3-0.5$ s, where $\gamma_{n.c}$ is the coagulation constant for nanometer-sized particles which is approximately equal to $5 \cdot 10^{-10}$ cm^3/s . In these approximations, the equilibrium number and mass concentrations of neutral clusters $N_{n.c}$ and $M_{n.c}$ in air are estimated to be rather essential:

$$\begin{aligned} N_{n.c} &\approx (q_i / \gamma_{n.c})^{1/2} = 5 \cdot 10^9 \text{ cm}^{-3}, \\ M_{n.c} &\approx 2N_{n.c}m_i \sim 1 \text{ } \mu\text{g/m}^3 \end{aligned} \quad (1)$$

where m_i is the mass of the light-weighted ion, approximately equal to $(1-2) \cdot 10^{-22}$ g.

Primary middle-weighted ions are formed after collisions of neutral clusters with light-weighted ions [1]. The charge of the primary ions is equal to unity; their mean diameter is $D_{\pm} = 2.5-3.5$ nm (see Fig. 2). The time of formation of a middle-weighted ion τ_{\pm} may be estimated in the kinetic approximation using the known equation: $\tau_{\pm} \sim (\pi c_i D_{n.c}^2 N_{n.c} / 4)^{-1} = 0.2-0.5$ s, where c_i is thermal velocity of the light-weighted ion, equal to $3 \cdot 10^4$ cm/s , $D_{n.c}$ is the cluster diameter which is equal to $2 \cdot 10^{-7}$ cm.

On the basis of the recombination equation $N_{\pm} \sim (n_i / \alpha_{\pm} \tau_{\pm})^{1/2}$, one can easily estimate the equilibrium number concentration $N_{\pm} = 3 \cdot 10^7$ cm^{-3} and mass concentration of the middle-weighted ions:

$$M_{\pm} \approx 3N_{\pm}m_i \sim 10^{-2} \text{ } \mu\text{g/m}^3 \quad (2)$$

where n_i is the current concentration of light-weighted ions, which is approximately equal to 10^8 cm^{-3} , α_c is the constant of recombination (association) of middle-weighted ions [15] which is equal to $(2-4) \cdot 10^{-7}$ cm^3/s .

Differently charged middle-weighted ions also associate rather rapidly due to Coulomb forces

and form neutral particles with a size $D = 5\text{--}10$ nm; these particles can be detected by electric analyzers. In general, middle-weighted ions occupy a band of mobility from 1 to $0.01\text{ cm}^2/(\text{V} \cdot \text{s})$ with two well-resolved modes at 0.1 and $0.05\text{ cm}^2/(\text{V} \cdot \text{s})$ [1, 20].

Thus, a result of collisions of light and middle ions, and also as a result of nucleation processes [21], rather stable aerosol particles are formed. Their concentration and particle size distribution are determined by the energy contribution into the ionizer:

$$E = I\varepsilon_i t_{i,r} / (Be) \quad (3)$$

where $\varepsilon_i = 15\text{ eV}$ is energy consumed for the formation of a molecular ion, $t_{i,r}$ is irradiation time, B is ionizer volume. The diagram shown in Fig. 2 was obtained for the ionization source with the current strength $I = 1\text{ }\mu\text{A}$, so for irradiation time $t_{i,r} = 6\text{ s}$ minimal energy contribution will be $\sim 10^{12}\text{ eV/cm}^3$.

Within the admissions accepted here, it is interesting to estimate specific productivity W_{max} of the synthesis of aerosol matter with an ideal ionizer, that is, assuming that all the light ions generated take part in the formation of the aerosol. Keeping in mind that the number of all the molecules in an aged light ion can reach $m^* = 4\text{--}6$, we obtain an estimated value $W_{\text{max}} = m^*/\varepsilon_i$ approximately equal to $25\text{--}40$ molecules / 100 eV . Below we will demonstrate that under normal atmospheric conditions $W = 5\text{--}10$ molecules / 100 eV .

Let us turn to the results of analysis of the chemical composition of gaseous and aerosol products obtained under intense ionization of dust-free air in a 400-cm^3 volume.

The concentration of nitrogen oxides in the flow ionizer with the energy contribution $E \sim 10^{12}\text{ eV}$ from the radiation source based on Pu-239 is, $\mu\text{g/m}^3$: in aerosol, $1.7 \pm 0.2\text{ NO}_2$, $1.1 \pm 0.1\text{ NO}$; in the gas phase, $16 \pm 2\text{ NO}_x$. Total concentration of NO_2 and NO oxides in the condensate reaches $\sim 3\text{ }\mu\text{g/m}^3$. Keeping in mind that within the above-presented physical model each light ion based on nitrogen oxides binds $3\text{--}5$ water vapour molecules, depending on the state of the air, one can easily obtain a theoretical estimation of the specific mass of the condensate concentrated on light ions: $M^* = Mm = 10\text{--}15\text{ }\mu\text{g/m}^3$. It will be shown below

(see Fig. 2) that this estimated value corresponds to M_a observed for intensive ionization under natural conditions: $2\text{--}20\text{ }\mu\text{g/m}^3$.

The concentrations of nitrogen oxides in the gas phase in the ionizer turn out to be substantial ($914\text{--}18\text{ }\mu\text{g/m}^3$), in particular, in comparison with their concentrations in the surface air layer: $[\text{NO}_2] \sim 1\text{--}5\text{ ppb}$ ($1\text{ ppb} = 1.88\text{ }\mu\text{g/m}^3$), $[\text{NO}] \sim 0.1\text{--}1\text{ ppb}$ ($1\text{ ppb} = 1.23\text{ }\mu\text{g/m}^3$) [21]. Correspondingly, it is reasonable to estimate the degree of acidity and hygroscopicity of the formed radiolytic aerosol and to consider the possibility of condensation processes to occur in the ionizer.

It has already been noted above that the particles of the nanometer-scale size in predominant concentrations are formed at the first stage of ionization. In fact, they are microdroplets of nitric acid. According to [21], water in the clusters containing more than 45 H_2O molecules (which corresponds to the particle diameter about and above 1.5 nm) exhibits the properties characteristic of the liquid state. Chemical activity of the clusters, in particular their acid properties, will be determined by the dissociation degree of HNO_3 molecules. It is known that the dissociation degree of 62% (so-called technical-grade) nitric acid does not exceed 9.6%. In the case under consideration, when there are $3\text{--}5$ water molecules in a cluster per one nitric acid molecule, the concentration of the solution should be within the range $10.5\text{--}8\text{ mol/l}$. The corresponding dissociation degree is $10\text{--}12\%$, so the solution under consideration is only partially dissociated. This circumstance brings substantial complications into the analysis of electrostatic interactions between nanoparticles and the surrounding ions; these interactions to a substantial extent define the rates of charge and mass transfer in the system [22].

Hygroscopicity of the new nanoparticles is determined by the ratio P/P_∞ , where P is water vapour pressure near the particle surface, P_∞ is pressure of saturated water vapour at infinity. According to the estimations using the known Thomson-Kelvin equation, for single-charged and neutral particles 10 nm in diameter, the ratio is equal to $1.1\text{--}1.4$. The latter means that the hygroscopic properties of the formed nanoparticles would not be exhibited noticeably.

So, bipolarly ionized air under the energy contribution about $10^{12}\text{--}10^{14}\text{ eV/cm}^3$ contains

increased amounts of ozone and nitrogen oxides, light-weighted ions 0.8–1.2 nm in diameter, neutral cluster with the diameter of 1.5–2 nm, middle ions 2.5–3.5 nm in diameter, and aerosol particles with the diameter 3–10 nm and more. The prevailing material of the ions and aerosol particles is weakly dissociated aqueous solution of nitric acid. The key mechanism of the formation of the new aerosol material is the coulomb association of heteropolar light ions.

ROLE OF GEOGRAPHIC AND METEOROLOGICAL FACTORS

In order to estimate the geographic and meteorological factors, we carried out measurements of the disperse composition of aerosol at the outlet of the ionizer in 1986–1990 in the regions with continental, marine, mountainous and arid climate (see Fig. 1). The results of measurements are generalized in Fig. 3. For comparison, the same figure shows the calculated concentration of the maximal total volume concentrations of the radiolytic aerosol at the outlet of the ionizer as a function of its characteristics

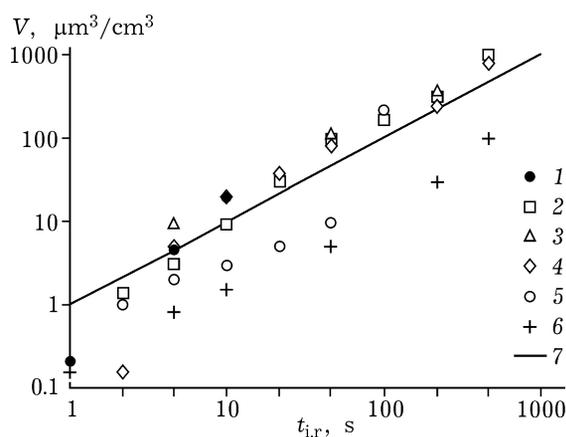


Fig. 3. Volume concentration of aerosol (V) as a function of irradiation time t_{ir} for air ionization with the radiation of Pu-239 isotope ($I = 1 \mu A$) in different regions: 1 - mountains (Pamir, 3000 m, September 1989, $T = (10 \pm 10)^\circ C$, $H = (50 \pm 20)\%$); 2 - sea (the Kola Bay, December 1989, $T = (-7 \pm 3)^\circ C$, $H = (70 \pm 20)\%$); 3 - forest-steppe (Ukraine, the region of Chernobyl APP, June 1986 and June 1987); 4 - desert (Tajikistan, September 1989, $T = (25 \pm 3)^\circ C$, $H = (30 \pm 10)\%$); 5 - forest (near Obninsk, June 1986, $T = (20 \pm 5)^\circ C$, $H = (70 \pm 20)\%$); 6 - motor road (near Obninsk, March 1986, $T = (5 \pm 3)^\circ C$, $H = (80 \pm 10)\%$); 7 - calculation according to equation (4).

$$V[\mu m^3/cm^3] = 2 \cdot 10^{-12} I m_i t_{ir} / (e B \rho_a) \quad (4)$$

where ρ_a is the density of the aerosol material; it is approximately equal to 1.5 g/cm^3 ; t_{ir} is irradiation time, or time of the action of radiation, which is equal to 1–1000 s.

The functional dependencies $V(t_{ir})$ observed in Fig. 3 can be formally bound as a first approximation to the action of geographical factors, namely:

1. In the regions with mountainous, steppe and marine climate the measured volume concentrations of the new aerosol (V) for irradiation time more than 10 s are grouped near the calculated straight line built up according to the physical model (4). According to this model, the aerosol material is formed without losses as a result of Coulomb association of light ions of different polarity. It is important that in remote measurement areas the effect of seasonal factors and local meteorological conditions was insignificant.

2. In vegetating forests near Moscow and along roads, the value of V turned out to be ten times smaller than the optimal value.

3. For short irradiation time ($t_{ir} < 10 \text{ s}$), the yield of radiolytic aerosol was most frequently smaller in comparison with the optimal value and was independent of measurement region. In this situation, the effect of meteorological conditions with respect to temperature and relative humidity was substantial.

Instrumental analysis showed that at the areas of the first group (s. 1) the concentrations of hydrocarbons in the air were usually not higher than the mean global level. Hydrocarbon concentration in the areas of the second group was 5–10 times higher. A possible explanation of the inhibiting effect of some hydrocarbons can be the known fact that alkanes form an efficient sink for nitrogen oxides. For example, a known process is the reaction of excited NO_2 molecules with alkyl radicals CH_3 formed in the radiolysis of a number of complicated hydrocarbons: $\text{CH}_3 + \text{NO}_2 \rightarrow \text{CH}_3\text{O} + \text{NO}$. As a result, the concentration of NO_2 molecules decreases. When the ionizer operates for a long time, a proper radiochemical mechanism of the production of nitrogen oxides starts to work, so the effect of many external factors on the efficiency of radiolysis is leveled.

In general, taking into account the errors of determination of ion current $\pm 25\%$ and the errors of measurement of aerosol dispersity $\pm 20\%$, there are reasons to conclude that dependence (4) obtained within the recombination model provides rather adequate description of the formation of radiolytic aerosol under irradiation time from 10 to 10^3 s.

CONCLUSIONS

1. Intensive ionization of the air results in substantial modification of its ion, aerosol and gas composition. For example, in a flow ionizer based on isotope plutonium-239 (activity: $400 \mu\text{Cu}$, irradiation time 5–10 s), concentrations of ozone, nitrogen oxides and nitric oxide vapour increase by a factor of several tens. The concentrations of light- and middle-weighted ions of both polarities increase from 10^3 and 10^2 cm^{-3} to 10^9 and 10^7 cm^{-3} , respectively. Non-volatile aerosol particles of the nanometer size are formed: $D = 3\text{--}10 \text{ nm}$. Their mass concentration reaches $3\text{--}5 \mu\text{g}/\text{m}^3$, and number concentration is $10^6\text{--}10^7 \text{ cm}^{-3}$ and higher, that is, exceeds the level characteristic of the surface air layer by a factor of a thousand or more times.

2. The new particles are mainly microdroplets of the aqueous solution of nitric acid.

3. In the air of remote marine, mountainous and arid regions, with the energy contribution into the ionized volume from 10^1 to $10^{14} \text{ eV}/\text{cm}^3$, the mass concentration of the new aerosol increases according to the linear law from 50 to $5000 \mu\text{g}/\text{m}^3$ with an increase in irradiation time from 10 to 1000 s.

4. Under optimal atmospheric conditions, the degree of conversion "irradiation–condensate" reaches 5–10 molecules/100 eV. This means that the surface air layer possesses substantial resources for ion-stimulated generation of the aerosol matter.

5. The model of the radiolytic aerosol as a product of association of light-weighted atmospheric ions of different polarity with the formation of neutral clusters and middle-weighted ions provides an adequate description of the field experiment.

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