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NEW CONTROLLING METHODS OF THE OZONE CONCENTRATION IN THE ATMOSPHERIC AIR

Abstract. Basic principles are expounded and prospects of application of homopolar corona charge on microelectrodes (microwire, needles and etc.) for development of methods and methods of control of concentration of ozone in atmospheric air. Investigational and described ozonometers descriptions corona charge, based on distinction of values of to mobility of ions of different arctic ions in the external zone of charge. Constructions over and technical descriptions of small ozonometers are brought, worked out on the basis of corona charge. For this aim the existing dependence of the middle mobility of ions is used in the zone of corona digit from the concentration of ozone in atmospheric air, coming from outside. Ozonemeters built on this principle work on a balancing network comparing average mobility of ions in two chambers during entering of ozone into charge zone. In other device for control of ozone concentration two charge intervals are used with the volume charges of different polarity, which appear between the corone needles and external electrodes, combined with ozone swallowers from porous silicagel. The ozonometer is based on the impulse-mode of negative crown, which determines the concentration of ozone in atmospheric air based on current of crown.

Keywords: corona charge, microelectrode, ozone, mobility of ions, balancing network, impulse mode, electronic avalanches.

Introduction. Measuring of concentrations of ozone has an actual value for physical and chemical features of ozone and technology of ozone production and continuous control of amount of ozone in the air is also needed in ozone treatment of domestic and official premises apartments and curative chambers and hospitals. In all cases ozone measuring devices are required to be simple in their constructions and comfortable during operations with high noise immunity and accuracy in measuring [1].

Well-known methods and devices for control and determination of concentrations of ozone in the air and based on iodide metrical, interferometrical and photometrical methods are in most cases stationary devices and differ with complicated performance and inconvenience. A classic iodine metrical method is also labor intensive during realization of control of ozone and does not provide continuity of measuring [2].

Presently there are several hundred methods of analysis and control of ozone.Conditionally they can be divided into physical, physical and chemical and chemical.

Based on other classification it is possible to divide into absolute and relative. The first ones allow directly to get the size of measureable concentration; the most accurate from them can serve as primary standards, based on which the calibration of ozonemeters are performed; the second ones measure a size, and being the function of concentration of ozone, they themselves require to be calibrated.

The problem of creation of method of control of ozone and development of the devices for its realization was set, and those differed from well-known methods with its high exactness and reliability of measuring at simplicity and comfort in-process. The results of researches showed that the most effective way for measuring of concentrations of ozone in atmospheric air there is the determination of them through to mobility of ions in a corona discharge.

Method of control of concentration of ozone in the air. When the analysis of well-known data and measured values of mobility of different sorts of ions is executed in the zone of unipolar corona, and also the processes of formation and loss of atomic and molecular ions of oxygen and nitrogen in corona are considered, we must define ozone metrical descriptions of corona charge. For this aim is used the existing dependence of middle mobility of ions in the zone of corona from the concentration of ozone acting from outside. Meantime, developed ozone meters [3] work according to balancing network by comparison of change of middle mobility of ions in the negative and positive corona at entering of ozone into the zone of charge from outside. Therefore it is necessary to consider the mechanisms of influence of entering ozone and kinetics of change of middle mobility of ions for different polarity of crown on individual basis.

It is necessary noted that middle mobility of ions grows also, when mobility of separate sorts of ions grows. Therefore, we have to consider separate elementary processes that lead to the increase of mobility of the ions during entering of ozone from outside.

In the negative corona the reactions of transformation of atoms, molecules and ions of oxygen (table) are related to the basic elementary processes.

Reactions leading to the increase or to the decrease of k_{cp}

#	Increase k_{cp}	Reduction k_{cp}
1	$O_3 + O_2^- \rightarrow O_2 + O_3^-$	$O_3 + O^- \rightarrow O + O_3^-$
2	$O_3^- + N_2 \rightarrow O^- + O_2 + N_2$	$O_3 + O \rightarrow 2O_2$
3	$O_3 + O_2 \rightarrow O_2 + O + O_2$	
4	$O_3 + O(D) \rightarrow O_2 + O + O$	
5	$O_3 + O_2\left({}^1\sum_d^+\right) \rightarrow 2O_2 + O$	
6	$O_3 + O_2\left({}^{\prime}\Delta d\right) \rightarrow 2O_2 + O$	

In terms of data of the table and taking into account other well-known reactions, the table shows two groups of reactions that conduce to the increase or to reduction of middle mobility of ions in the zone of corona charge, when ozone comes from outside.

As follows from this table, at the receipt of ozone from outside majority of reaction lead to the increase of k_{cp}, which is related to formation of atomic oxygen and its ions, having higher mobility. In addition, the reactions of ozone are presented with atoms and molecules of oxygen, which have the different electronic states. It should be noted, last reactions with ozone take course, mainly, in a corona layer or on its border.

Now we will consider molecular processes, processes running during interacting of ozone with the ions of nitrogen and oxygen in the external area of positive corona charge.

As is generally known, basic carriers in a positive corona charge are O^+, O_2^+, N^+, N_2^+, that co-operate with the molecules of ozone, acting from outside, as follows

$$O^+ + O_3 \longrightarrow O_2^+ + O_2, \qquad (1)$$

$$N^+ + O_3 \longrightarrow NO^+ + O_2, \qquad (2)$$

$$O_2^+ + O_3 \longrightarrow O_2 + O_3^+, \qquad (3)$$

$$N_2^+ + O_3 \longrightarrow N_2^+O + O_2^+. \qquad (4)$$

If to take into account the values of mobility of former and newly formed ions (O^+ -3,2; O_2^+ -2,24: O_3^+ -2,54: N^+ -3,3: N_2^+ -1,87: NO^+ -1,96 см/В.с), it is obvious, that reactions (1) conduce to reduction, and reactions (2-3) to the increase of middle mobility of ions in the external area of corona charge [4]. Considering that reactions (1) take place only in a narrow area near-by corona electrode, and therefore their contribution into the general charge current is insignificant, while reactions (2-3) flow in the external area of corona charge and bring in a substantial contribution to the general charge current. Considering the direct dependence of the current charge size on the value of middle mobility of ions it appears the possibility to define the volume concentration of ozone within the charge intervals based on increase of the current.

For the purpose of increase of accuracy of control and reliability of results, the balancing network of measuring is used, one of shoulders of which is the second charge interval, where air stream purged from ozone gets through a damper chamber (ozone absorber), and at that the other shoulder is the first charge interval in its primary kind. Thus, comparison of two charge currents and measuring of them on the difference of potentials of tensions on loading of charge intervals, allows substantially decrease the errors of ozone control due to the change of electric descriptions of charge, temperature and pressure of gas, and also from a current rate. Since the charge current of the first charge interval changes in direct ratio to the changes of concentration of ozone in ozone containing air, then it is not difficult to carry out calibrating of output device on the beforehand well-known concentrations of ozone in the air [5].

A damper chamber (ozone absorber) serves for cleaning of air stream from remaining ozone, prior it gets in the second area of the charge. Meantime a damper chamber (ozone absorber) does not render substantial influence on other gas mixtures in a stream, and in connection with this their affecting on charge description of measuring intervals is mutually compensated. One of variants of implementation of damper chamber is the using as a reactionary zone for ozone of positive volume charge of corona charge.

In other variant, as ozone absorber can be used the natural absorbers of ozone (porous rubber, absorbent carbon, oxides of iron, copper shaving etc.), which also during their setting must meet the condition of "transparency" for other gases of stream.

On figure 1 the functional diagram of device is presented for control of ozone in mid air.

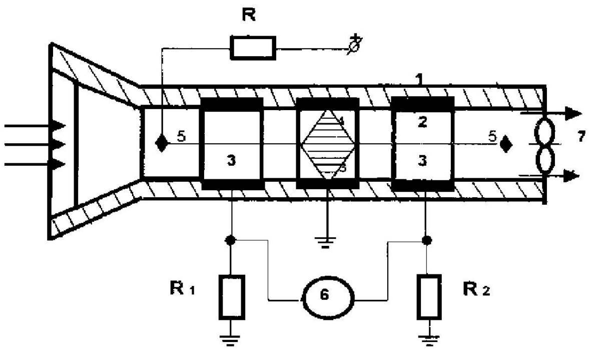

Figure 1 – Device for control of ozone in the air

The developed device contains a corps from dielectric material 1, corona wire 2 and external metallic electrodes in the cylinders form 3. In our case as the ozone absorber it is used the positive volume charge of corona charge 4. Corona wire 2 is fixed from two ends by holders 5 and then, through ballast resistance of R connected with the positive pole of power supply. External metallic electrodes 3 of the device are earthed: the external electrode of damper chamber should be earthed at once, and external electrodes of two charge intervals through loading resistances of R_1 and R_2. Output device 6 is added to the alarm points of resistances of R_1 and R_2. In order to create the even stream of ozone containing air through the devices it is used an air-exhauster 7.

During delivery of high enough tension on a wire, between it and external electrodes appears corona charge, which is the unipolar form of charge. Whereupon, by means of air-exhauster the air in which the ozone amount is measured, is driven away through a device, where it interacts by turns with the positive volume charges of discharge intervals. Along with it, the value of potentials difference of tensions on loading of two charge intervals, registered by an output device in fact will correspond to the concentration of ozone in surrounding air. The offered device differs with simplicity and comfort in work, provides noninertia and continuity of measuring. Besides, calibrating of output device and choice of the range measuring are to be performed only once.

A device has the following parameters: diameter of the corona electrode of 50 microns, external electrodes in the form of cylinders have the diameter of 10mm, tensions of power supply can change in a range from 3,2 to 4,4кВ. The mode of positive corona charge is created in measuring charge chambers. For the control measuring as the source of ozone a charge chamber with a negative corona with the exit of ozone from 2 to 10mg per hour at atmospheric pressure was used. Tests showed that an offered device at its simplicity of construction has a sufficient sensitiveness to ozone (from 0,2 to 0,25mg/mkA) and can be used as an indicator of ozone in domestic and economic terms [3].

Device for ozone concentration control. The processes of interaction of molecules of ozone with the ions of O_2^+ and N_2^+ and subsequent formation of secondary ions of O_3^+ and O_2^+, on the whole, lead to the increase of middle mobility of ions in the external zone of corona charge and accordingly, to the increase of size of current of charge. Thus, skipping ozone containing gas through the first discharge interval, and then through a damper chamber – (ozone absorber) the second discharge interval and comparing discharge currents on their loading it is possible to determine the concentration of ozone in ozone containing gas. Thus, some attractiveness of application of positive corona charge takes place for the aims of control, because it has an ozone energy effect, which is more lower than the negative corona charge. In addition, the application of damper chamber – ozone absorber, allows to get the gas and the air on the exit of device, purged from ozone.

During flowing of negative charge, there are the ions of O^-, O_2^- and O_3^-, in the external area, which take part in the processes of recharge of ions, and at that, ions of O_2^- and O_3^- are responsible for passing of discharge current, although in accordance with their amounts, O_2^- - to a greater degree, O_3^- – to a lesser degree. Appearance of foreign ozone substantially changes character of processes of recharge of ions in the external area of discharge, because ozone has higher energy of affinity to the electron as compared to O (1,4) and O_2 (1,45). In this case, the portion of ozone as a carrier of charges into the external area of charge increases in accordance with the its concentration in a gas analyzed.

If to take into account the values of mobility of molecules of oxygen (2,24 $см^2$/В-с) and ozone (2,54), then it is necessary to expect the increase of middle mobility of ions in the external area of corona charge. All that, on the whole, results in the increase of deposit of ions of ozone in a general discharge current, which is the basis of use of corona charge in order to control the concentration of ozone in a ozone containing gas.

In an offered device it is used two discharge intervals with the by volume charges of different polarity, which are formed between the corona needles and external electrodes, combined with ozone absorbers from porous silica gel. Considering that, corona needles are directed to the opposite sides, external electrodes having forms of the ozone absorbers, are located symmetrically on the different ends of dielectric tube. If ozone absorber for a negative corona charge is used for neutralization of ozone, then for a positive corona charge, besides, it serves for the observance of requirements of identity of two discharge chambers [6].

Input of ozone containing gas into an ozonometer is performed through the holes in a dielectric tube, located on equal distance from discharge intervals. In the process of work of ozonometer between corona needles and external electrodes there is electric wind with speed no less than 1-3 m/s, which renders through holes the suction effect on air of ambient air. Here main is a process of draw of air for control from one area of ambient air, which leads to identity of composition of air in discharge intervals in part of presence of admixtures and aerosol particles.

In addition, combination of external electrodes with ozone absorbers and situation without a ventilator, on the whole, conduces to simplicity of construction and absence of additional devices , which are necessary for work of ozonometer. The balancing network of measuring also allows substantially to bring down the errors of control of ozone, appearing due to the existing difference of electric descriptions of bipolar discharge intervals.

Application of bipolar power supply provides determination of difference of currents, running in the discharge intervals, which is proportional to the concentration of ozone. At such possibility of measuring of overfall of tension of negative polarity on the general loading, it is created the condition to use of ozonometer in ATSS and adjusting of concentrations of ozone in the working atmosphere of premises.

Zeroing, when there is lack of ozone and calibrating of scale of output device on the well-known concentrations of ozone in mid air is performed by means of balancing network.

On the figure 2 the functional diagram of ozonometer is presented with the bipolar power of supply 1.

An ozonometer works as follows. During delivery of high tension from the bipolar power of supply on corona electrodes 5, between them and external electrodes 6 there are bipolar corona charge, which create the electric winds directed to the opposite parties.

After establishment of stable electric wind in discharge intervals (no more than 5 sec) the principle of ion-convection pump starts to work, providing suction effect going through the holes 4 outward airs (ozone containing gas) into ozonometer, which simultaneously will pass through discharge intervals for control of ozone. Initially, during the lack of ozone in outward air, with the help of R_2 the readout of output device 7 hatches on a zero. At that, the existing difference is also compensated in electric descriptions of positive and negative corona charges in the discharge intervals of ozonometer, and due to the application of balancing network of measuring of influence on accuracy of control of admixtures or other aerosol particles, presence of which in ozone containing gas is not eliminated, also is taken to the minimum.

Thus, the value of difference of currents from two discharge chambers 2a depends upon the concentration of ozone parameter in an ozonometer, which registers itself as an output device 7 or passed to SAC (system of automatic control). If the sensitiveness of ozonometer to ozone depends on the steepness

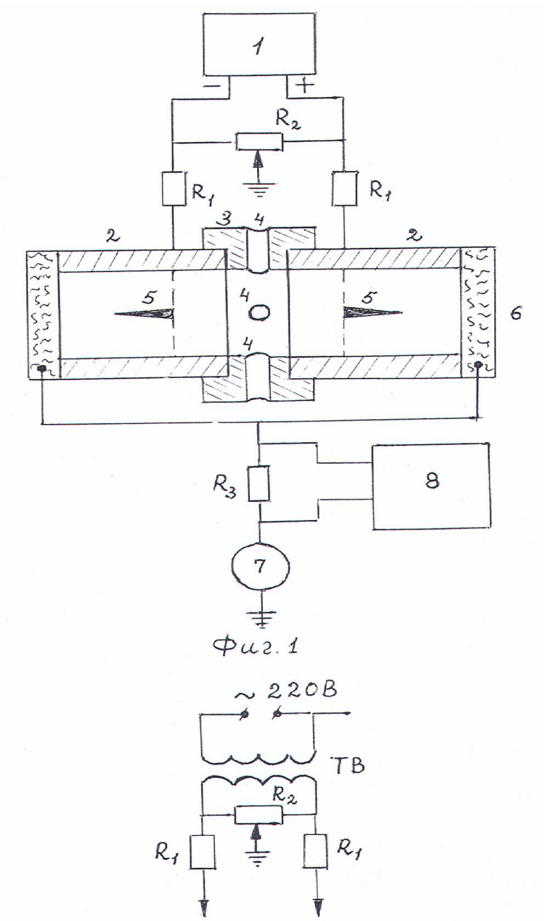

Figure2 – Functional diagram of ozonometer

of descriptions of corona charges, then accuracy of control of ozone will depend on stability of tension of power of supply and constancy of geometrical parameters of discharge intervals. The steepness of descriptions of corona charges, in turn, is determined by the value of high tension and geometry of discharge intervals (by the radius of curvature of corona needle and inter-electrode distance).

The body of ozonometer, consisting of three parts (2,3) fixed with each other on axes basis is made from a fluoroplastic, and at that internal diameter of tubes 2 makes a 20 mm, and length is 30 мм. In tubes 2 there are axisymmetrical located 5corona needles, pressed-on on thin nets from a nichrome. Corona needle is made from a thin molybdenum wire (d=a 0,5 mm) with the radius of rounding on an edge about 0,2 мм. External electrodes –ozone absorbers are made from porous silica gel with a metal-backer surface with a thickness 5 мм. They are "transparent" enough for passing of air under the action of electric wind.

An ozonometer provides automatic control of ozone in a working atmosphere at a high sensitiveness and reliability of results of measuring, which is arrived at simplicity of construction and lack of additional adaptations. It can be used in ozone equipment and at ozone treatment of domestic, official and production premises [6].

On a figure 3 the functional diagram of device for control of concentrations of ozone is presented.

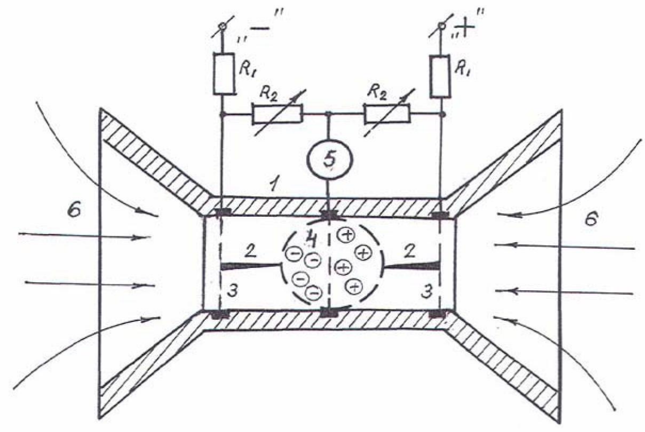

Figure – Functional diagram of device for ozone concentrations control

A device contains a corps from dielectric material 1, corona electrodes consisting of corona needles 2, which fixed on axes basis with a corps 1 fastened to the net. Corona needles 2 through ballast resistances of R_1 to the different poles of power supply [7].

External electrode 4, performed as a metallic net and being general for both discharge intervals, unites through an output device 5 and regulative resistances of R - 2 with the poles of power supply. After connection of high tension and appearance of corona charge in discharge intervals in the swept volume electric wind appears 6 in the direction of edge of corona needles 2.

A device works as follows. At the serve of the high enough tension in the first discharge interval, made from a corona needle 2 and external electrode 4, there is a negative corona charge, while a positive corona charge takes place in the second discharge interval. After a while (no more 5sec.) in that and in other case in discharge intervals electric winds appear 6, directed against each other.

Impulsive ozonemeters. A method will be realized in a device, containing corona and external electrodes, between which a negative corona charge is created and unlike well-known it contains stabilizator of current in the chain of discharge current and amplitude discriminator in a measuring chain, serving for the exception of bearing frequency of impulses of Trichell.

For substantial reduction of influence on accuracy of measuring of vibrations of discharge parameters the stabilizator of current is used, in order to stabilize a discharge current at the possible changes of tension of power supply, pressure and temperature of air. Stabilizing of current of charge, in uts turn, results in stability of amplitude and frequency of impulses of trichell, while dependence of them on the admixture of ozone in mid air remains the same.

It is determined that of all impulses of Trichell the overwhelming ones on a closeness (bearing frequency) are those impulses that got beginning from the electronic avalanches of the first echelon, arising up and getting development from the surface of corona electrode. It was found that there is a direct dependence of amplitude of Trichell impulses of bearing frequency on the radius of curvature of corona electrode, which served as the basis for development of method of control of micro wire diameter [8]. Meantime, in our case, the presence of Trichell impulses of bearing frequency in the process of measuring sharply reduces accuracy of control of concentrations of ozone on an offered method.

In order to except the bearing frequency of Trichell impulses it is used an amplitude discriminator in the measuring chain of device, which limiting on amplitude and chopping off the Trichell impulses of bearing frequency, skips for measuring only such impulses that are the result of electronic avalanches of the second echelon, arising up on the border of corona layer of charge. Now in the process of measuring will take part only those impulses of Trichell, that appeared from secondary electronic avalanches in the corona layer of charge. Thus, totality of substantial signs allows substantially to increase the measuring accuracy and to get the reliable results at control of concentration of ozone in mid air [9].

A device works as follows. At the serve of high enough tension to negative polarity on a micro wire, between it and a cylinder is a unipolar charge in the pulse-mode (Trichell impulses), that is characteristically for a negative crown from the micro wire.Tension of power supply at ballast resistance of 100 мОм was 10 кВ (a cylinder is a 10 mm, micro wire is 50 microns). A midfrequency of Trichell impulses in lack of admixtures of ozone in mid air was 140 kHz, strength of discharge current - 40 мсА. Because of absence of the calibrated generator of ozone the calibrating of device on the concentration of ozone was not produced. Meantime, in our case, the presence of Trichell impulses of bearing frequency in the process of measuring sharply reduces accuracy of control of concentrations of ozone on an offered method.

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Tension of power supply at ballast resistance of 100 мОм was 10 кВ (a cylinder is a 10 mm, micro wire is 50 microns). A midfrequency of Trichell impulses in lack of admixtures of ozone in mid air was 140 kHz, strength of discharge current - 40 мсА. Because of absence of the calibrated generator of ozone the calibrating of device on the concentration of ozone was not produced. Meantime, the analysis of the obtained data and calculations of electric descriptions of device shows that the offered method as compared to well-known one provides the increase of measuring accuracy in several times.

A device, carrying out control of concentration of ozone, is electrodes as a net metallic cylinder (5-10мм) and micro wire made of tungsten (50-100 microns) and strained on its axis, on which permanent tension of negative polarity (5-10 кВ) is given.

To create the waiting mode of charge as usual, it is used ballast resistance of sufficient size (to 100 мОм), and to external electrode is connected with loading resistance and integrating chain with the electronic voltmeter of direct-current.

On a figure 4 the functional diagram of device is presented to control the concentration of ozone.

A device contains a corps from dielectric material 1, four plates also made of insulating material 2 to fasten the net electrode 3 and corona electrode as a micro wire made of tungsten 4. Corona electrode is connected through ballast resistance of Rt with the power module 5. External electrode 3 is earthed through loading resistance of R2, to which integrating chainlet of R3C and electronic voltmeter of direct-current 6 is connected.

The device works as follows. At the serve of high enough tension to negative polarity on a micro wire, between it and a cylinder it appears unipolar charge in the pulse-mode (impulses of Trichell), which

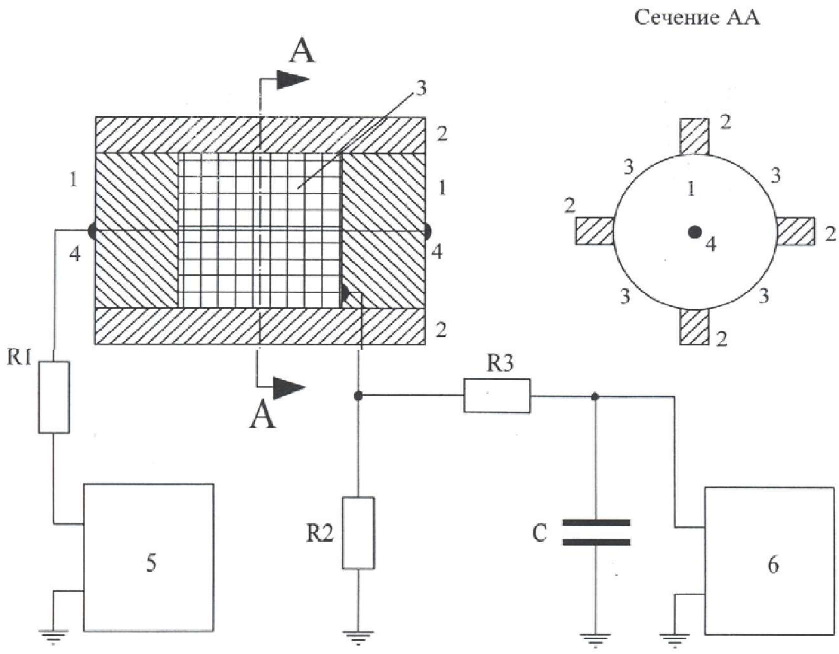

Figure 4 – Functional diagram of device for control concentration of ozone

is characteristically for a negative crown from a micro wire. In order to achieve the waiting mode of corona charge at these geometrical parameters of electrodes (cylinder -10 mm, length-20 mm, micro wire-50 microns) regulate high tension setting a discharge current no more 1мкА.

In connection with absence of the calibrated generator of ozone the calibrating of scale of output device on the concentration of ozone was not executed. Tests showed that an offered device had a high sensitiveness to ozone (to 0,1 mg/of мВ) and can be used as check device in shopfloors.

Conclusions. The new methods of control of ozone are created and worked out a number of modification of ozonemeters based on existent ozonemetrical descriptions of corona charge. The results of researches and approbations of the worked out devices showed on the difference of them from known ones for the high accuracy and reliability of measuring at a simplicity and comfort in-process.

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АТМОСФЕРАЛЫҚ АУАДА ОЗОН КОНЦЕНТРАЦИЯСЫН БАҚЫЛАУДЫҢ ЖАҢА ӘДІСТЕРІ

Аннотация. Атмосфералық ауадағы озон концентрациясын бақылау және қалыптастыру тәсілдерін оңтайластыру үшін, микроэлектродта (микросым, инелер және т.б.) униполярлы тәжді разрядтың бас принциптері және қолдану перспективалары көрсетілген. Сыртқы разрядта орналасқан әртүрлі полярлы иондардың қозғалғыштығының әртүрлілігінде негізделген тәжді разрядтың озонометриялық сипаттамалары зерттелген және түсіндірілген. Тәжді разрядтың негізінде жасалған кіші габаритті озонометрлердің құрылымдық және техникалық сипаттамалары берілген. Осы мақсат үшін атмосфералық ауадағы озон концентрациясының орта қозғалғышты иондардың тәжді разрядтың аймағындағы қазіргі уақытта белгілі тәуелділігі пайдаланылады. Озонометрлер разряд аймағының екі камерасына озон түсуіне байланысты орта қозғалғышты иондарды-баланс схемасы бойынша салыстыру арқылы жұмыс жасайды. Озон концентрациясын басқа құрылғыда бақылау үшін полярлығы әртүрлі екі қатарлы зарядты пайдаланылады,олар озонжұтқышпен біріктірілген тәжді инелермен және сыртқы электродтар арасында түзеді. Теріс тәждің импульстік режимінде негізделген озонометр, атмосфералық ауадағы озон концентрациясын тәж тоғының импульс жиілігімен анықтайды.

Тірек сөздер: тәжді разряд, микроэлектрод, озон, иондардың қозғалғыштығы, балансты сұлба, импулсті режим, электрондық ағындар.

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НОВЫЕ МЕТОДЫ КОНТРОЛЯ КОНЦЕНТРАЦИИ ОЗОНА В АТМОСФЕРНОМ ВОЗДУХЕ

Аннотация. Изложены основные принципы и перспективы применения униполярного коронного разряда на микроэлектродах (микропроволока, иглы и т. д.) для разработки методов и способов контроля концентрации озона в атмосферном воздухе. Исследованы и описаны озонометрические характеристики коронного разряда, основанные на различии значений подвижностей разнополярных ионов во внешней зоне разряда. Для этой цели используется существующая зависимость средней подвижности ионов в зоне коронного разряда от концентрации озона в атмосферном воздухе, поступающего извне. Озонометры, построенные по этому принципу работают по балансной схеме сравнивая средние подвижности ионов в двух камерах при поступлении озона в зону разряда. В другом устройстве для контроля концентрации озона используются два разрядных промежутка с объемными зарядами разной полярности, которые образуются между коронирующими иглами и внешними электродами, совмещенными с озонопоглотителями из пористого силикагеля. На импульсном режиме отрицательной короны основан озонометр, который концентрацию озона в атмосферном воздухе определяет по частоте импульсов тока короны.

Ключевые слова: коронный разряд, микроэлектрод, озон, подвижности ионов, балансная схема, импульсный режим, электронные лавины.