The problems associated with monitoring of main parameters of working areas and technological environments in high technology industry

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Abstract. Today, the matters of ensuring the safety of human life in a polluted environment, quality control of agricultural raw materials, food and the parameters of various environments is becoming increasingly urgent, especially in connection with the development of nanotechnology and nanoindustry. Therefore, high-precision measurements of aerosol parameters and the metrology of air weights are directly connected with the global problem of monitoring the safety of the use of nanotechnology. Since it’s been created the Russian State Primary Standard - GET 163 was modified two times to support the demanded measurement accuracy in this area in Russia. The standard has reproduced, maintained and transferred values of units of particle size, number particle concentration, mass concentration of aerosol particles, and, since 2020, units of electrophoretic mobility and zeta potential of particles in liquid media

1. Introduction and brief historical information
At the present stage of scientific and technological progress and the development of industrial production, the problem of ensuring the safety of human life in a polluted environment, the creation of environmental protection technologies and the disposal of man-made waste, quality control of agricultural raw materials and food products and the parameters of various environments is becoming increasingly urgent, especially in connection with the development of nanotechnology and nanoindustry. We emphasize the latter especially, because the production of products using nanotechnology is somehow connected with the impact on biological objects, hence the task of controlling the environment in which they are produced becomes extremely important in order to exclude the very possibility of a negative impact of both nanotechnology products themselves and nanotechnology processes on human health and the environment. Therefore, high-precision measurements of aerosol parameters and the metrology of air weights are directly connected with the global problem of monitoring the safety of the use of nanotechnology.

Aerosols are most widely used in the agro-industrial complex (plant protection, defoliation, fertilizing, disinfection, vaccination of animals, etc.), chemical industry, metallurgy, medical industry, building materials industry, etc. Here we can also name the work on the creation of "clean rooms" used in the production of pharmaceuticals and elements of modern microelectronics, where minimization and strict control of the number of particles in technological environments is necessary. Measurements of aerosol parameters are important for physical studies of the atmosphere (natural clouds, fogs, transcontinental dust transfers), in environmental studies, for environmental protection.
Such highly dispersed media as aerosols are used in almost all priority areas of modernization of the Russian economy: "Nanotechnologies and nanomaterials", "Technologies of mechatronics and creation of microsystem technology", "Technology of electronic component base creation", "Biomedical and veterinary technologies of life support, human and animal protection". Since the beginning of the 90s of the last century, the study of aerosol parameters (both radioactive and non-radioactive) began to occupy one of the leading places in the plans of scientific laboratories. The issue of the system of metrological support for measurements of dispersed parameters of aerosols has become acute.

To ensure the unity and reliability of measurements of aerosol parameters, it was necessary to develop a set of methods and tools that would reliably reproduce an aerosol with the specified parameters of dispersed composition and concentration, measure these parameters and transfer the parameter size to working measuring instruments with the smallest achievable error.

All-Russian Scientific Research Institute of Physicotechnical and Radio Engineering Measurements (VNIIFTRI), what had experience working with radioactive aerosols, were given the task to develop a system of metrological support for measurements of dispersed parameters of aerosols, hydrosols and suspensions.

After the approval of the installation UVT 91-A-97 created at VNIIFTRI, it was on the head of the Russian verification scheme for the particle counters MI 2507-98.

In the period from 1998 to 2003, using part of the UHT 91-A-97 equipment and the experience of its operation, VNIIFTRI developed the State Primary Standard of Units of Dispersed Parameters of Aerosols, Suspensions and Powdery Materials (GET 163), which was on the head of the corresponding Russian verification scheme, approved on June 26, 2003. The standard was intended to reproduce, maintain and transfer the units of particle size, counting and volumetric (mass) concentration, values of the particle size distribution function in aerosols, suspensions and powdery materials. The characteristics of the standard were determined for a spherical model of aerosol particles, suspension or powdery material.

The main disadvantage of the GET 163-2003 standard was that the lower limit of particle size measurement was limited to 0.5 microns, which did not meet the increased requirements.

In 2007, work was carried out at VNIIFTRI to improve the standard GET 163 – 2003 in order to expand the lower limit of the measurement range of particle sizes to 30 nm. The solution of this problem made it possible to carry out verification, calibration and testing of the entire fleet of modern highly sensitive instruments for measuring the dispersed parameters of aerosols and suspensions.

The standard with new metrological characteristics was approved as the Russian State Primary Standard of units of dispersed parameters of Aerosols, Suspensions and Powdery materials - GET 163-2010.

In 2011, interlaboratory comparison was carried out, in which leading laboratories participated in determining the dispersed parameters of aerosols from Europe and Australia: Griffith University (Australia), University Paris Est Creteil UPEC (France), Fraunhofer ITEM (Germany), TSI Gmbh (Germany), VNIIFTRI, NIFHI named after L.Y. Karpov.

2. Ensuring the uniformity of measurements and modernization of the primary standard

The main disadvantage of the standard GET 163 – 2010 was that the lower limit of particle size measurement is limited to 30 nm, which does not meet modern requirements. The need to reduce the lower limit of particle size measurement is related to the need for the development of the nanoindustry.

Since 2015, research has been carried out at VNIIFTRI to find solutions for improving the GET 163 – 2010 standard in order to expand the lower limit of the size measurement range to 1 nm, which allowed in 2017 to carry out work on improving GET 163-2010 [1-2].
Another urgent task of improving the GET 163-2010 was to expand the functionality of it in terms of reproducing another dispersed parameter - the zeta potential [3-4].

The zeta potential is a parameter that can be used to determine the long-term stability of suspensions and emulsions and to study surface morphology and adsorption on particles and other surfaces in contact with a liquid and depends on many factors and characteristics of the initial system.

The importance of determining the zeta potential is that its value is related to the stability of colloidal dispersions. The zeta potential determines the degree and nature of the interaction between the particles of a dispersed system.

For molecules and particles, a high zeta potential will mean stability, i.e. the solution or dispersion will be stable with respect to aggregation. When the zeta potential is low, the attraction exceeds the repulsion, and the stability of the dispersion will be violated. Thus, colloids with a high zeta potential are electrically stabilized, while colloids with a low zeta potential tend to coagulate or flocculate.

The creation of a system of metrological support for measurements of a unit of a specific quantity based on the primary state standard is justified given the wide demand for measurements of these quantities. The actual number of zeta potential meters built on the implementation of various principles (based on Doppler shift detection; direct visualization of the mass transfer front during electrophoresis; potentiometry) is estimated to be up to 3 thousand measuring devices (instruments). The market demand for such devices is estimated at the level of 15-17 thousand devices.

In 2012-2014, ISO international standards (13099-1, 13099-2 and 13099-3) [5-7] describing methods for determining the zeta potential were published. There were no regulatory documents on this type of measurement in Russia.

In the Russian market, devices for measuring the zeta potential are becoming increasingly widespread. Currently, there is no verification scheme for such measurements, tests for type approval and verification of such devices according to metrological characteristics related to the measurement of the zeta potential are not carried out.

In this regard, there was a need to ensure the uniformity of measurements of the zeta potential.

To achieve the required results, the methods for measuring the dispersed parameters of aerosol particles, suspensions and powdery materials used in GET 163-2010 were refined.

Currently, the main method of controlling the dustiness of the air of industrial premises and organized emissions is weight. This method is based on filtering dusty air through a particular filter, followed by a weight determination of the amount of dust caught. The disadvantages of the method are low productivity, the need to take into account the speed of air movement, its pulsation; the accuracy of the results depends on the quality of the filter and the qualifications of the researcher.

Indirect methods are based on the use of various physical phenomena, the parameters of which vary depending on the concentration of dust in the studied air. The advantages of indirect methods are high productivity, ease of measurement. Disadvantages - low measurement accuracy, design complexity and high cost of devices.

Optical, charge-contact, radioisotope, piezoelectric and capacitive methods are most widely used to control the dustiness of industrial premises and organized emissions, which are characterized by greater measurement accuracy and high sensitivity.

Acoustic, induction and other methods based on water dust capture have not been widely used due to low measurement accuracy, bulkiness and high cost.

To solve the problem associated with the lack of uniformity of measurements of the mass concentration of aerosol particles, combinations of methods were developed and implemented at VNIIFTRI:

- a reference set of equipment has been developed based on the joint work of the piezobalance method and the method of oscillating microweights,
- for an aerosol with known characteristics, a set of optical methods is used that allows measuring the particle size distribution function, mass and counting concentrations (including the particle mass concentration distribution function),
- enhanced diffusion aerosol spectrometer to measure the mass concentration of nanosized and submicron aerosols (including sinnesorgane),
- apparatus based on the method of differential electrical mobility, modified by the inclusion in the composition of its dual system of particle agglomeration, with the purpose of measuring the mass concentration of nano-disperse aerosols (PM 1- particulate matter with size smaller than 1 μm).

To measure the dispersion parameters of disperse nanoparticles in the environment are two methods of measurement.

This is the "differential mobility" method defined by the standard GOST R 8.775-2011 [8] and the method of diffusion aerosol spectroscopy according to GOST R 8.755-2011 [9].

The measurement of the parameters of the dispersed composition of particles by the method of "differential mobility" is carried out by separating particles by size and further registering the concentration of particles of this fraction. Particle size separation is carried out due to the dependence of the electrical mobility of the particles on the value of the electric field applied to the particles in the analyzer.

The separation of particles by charges is carried out using a so-called differential mobility analyzer. Before entering the differential mobility analyzer, aerosol particles pass through a "neutralizer", while achieving a stationary charge distribution.

After the differential mobility analyzer, the particles enter the condensation particle counter. In this case, monodisperse aerosol particles act as condensation nuclei of the superheated liquid, and after cooling are counted by an optical particle counter.

This method has been improved by the introduction of a "soft X-ray" neutralizer into the differential mobility system and the refinement of the condensation core counter by a "double enlargement" system, which made it possible to expand the boundary of the detected particles to 1 nm, as will be discussed below.

The method of diffusion spectroscopy is based on the determination of the particle diffusion coefficient by the measured value of the particle slip coefficient through the diffusion battery.

This method has been improved by the introduction of a submicron aerosol optical unit, an aerosol mass concentration measurement system and an additional enlargement unit into the diffusion aerosol spectrometer.

In the upgraded aerosol spectrometer, the condensation enlarger consists of two cascades. In the first cascade, condensation nuclei are enlarged from the minimum size to 10 nm, in the second, they grow to optically active sizes, when they can be analyzed by a laser particle counter.

In order to measure the particle size below the usual detection limit, the enlargement system was modified. This system measures particles with an aerodynamic diameter of 1 nm, which is highly in demand in science and industry for applications such as gas conversion into particles, synthesis of nanoparticles, nucleation nuclei formation and their growth, and burning emission research. The refinement consists in the use of an upgraded condensation core counter and the use of diethylene glycol (DEG) as a new working fluid for the preliminary growth of particles on which supersaturated steam will condense.

To measure the parameters of particles suspended in a liquid, the method of dynamic light scattering (DLS) (photon correlation spectroscopy) is used.

In the course of the work, the equipment for reproducing the zeta potential was manufactured, consisting of two main components:
- a system in which a combination of methods of phase analysis of scattered radiation (PALS) and electrophoretic light scattering (ELS) was implemented;
- a system in which the microelectrophoresis method was implemented.

The surface charge on a microscopic particle causes an electrical potential difference in millivolts between the surface of each colloid and the mass of the suspension liquid. This difference is called the "electrokinetic potential" ("zeta potential").
It is easy to measure, since the charged colloid will start moving when the suspension is placed between two electrodes, between which a direct current passes, and its speed will be proportional to the electrokinetic potential.

Electrokinetic potential measurements are carried out by a method called microelectrophoresis. To observe colloidal particles inside the chamber, called an electrophoretic cell, a high-quality stereoscopic microscope and a set of video optics are used. The electrodes located at each end of the chamber are connected to a power source, creating an electric field in the chamber. Charged colloids move in a field, and their speed and direction of movement are related to their electrokinetic potential.

The device first measures the electrophoretic mobility of the particles, which is expressed in "micron/second per volt/centimeter". The first term "micron/second" is a measure of speed, and the second term "volt/centimeter" is an expression of the strength of the electric field. The electrokinetic potential (in millivolts) is calculated based on the results of the measured electrophoretic mobility.

The developed cell configuration and the selected electrode material made it possible to measure the zeta potential of particles of different nature and different surface charge by applying voltage in a wide range (from 10 to 300 V). The developed cell configuration made it possible to adjust the response of the studied area in such a way that the error from the uneven velocities of the particle front will be excluded.

The metrological characteristics of the standard are presented in the table 1.

| Characteristic       | Measurement range       | $u_A$, % | $u_B$, % | $u_C$, % | $U (k=2)$, % |
|---------------------|------------------------|----------|----------|----------|--------------|
| Particle size       | from 0.001 to 0.03 μm   | 1.2...1.8| 0.7      | 1.3...1.9| 2.7...3.8    |
|                     | from 0.03 to 2000 μm    | 1.0...1.1| 0.6...0.7| 1.2      | 2.4          |
| Number concentration| from $10^3$ to $10^{12}$ m$^3$ | 1.5...1.7| 0.7      | 1.6...1.8| 3.2...3.6    |
| Mass concentration  | from 0.001 to 10 mg/m$^3$ | 0.9...1.7| 0.6...0.7| 1.1...1.9| 2.2...3.7    |
|                     | from 1 to 2000 mg/m$^3$  | 0.35     | 0.6      | 0.7      | 1.3          |
|                     | from 1 to 10000 mg/m$^3$ | 0.4...1.2| 0.6...0.8| 0.7...1.5| 1.3...2.9    |
| Electrophoretic mobility | from $-2\cdot10^{-7}$ to $+2\cdot10^{-7}$ m$^2$/(V·s) | 1.4...1.6| 0...0.8  | 1.5...1.7| 3.0...3.5    |
| Zeta potential      | from -150 to +150 mV    | 2.0...2.2| 0.9...1.0| 2.2...2.4| 4.4...4.8    |

3. Conclusion
Ensuring the uniformity and reliability of measurements in the field of measurements of dispersed parameters of aerosols and suspensions is in accordance with the Law of the Russian Federation "On ensuring the uniformity of measurements". The expansion of the measurement range of dispersed parameters of aerosols and suspensions meets modern requirements and the world level of development of this type of measurement and will allow you to transfer units of quantities to the secondary and working standards, carry out verification, calibration and testing in order to approve the type of the entire fleet of modern highly sensitive instruments for measuring dispersed parameters of aerosols and suspensions.

4. References
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