Development of industrial environmental control methods

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Abstract. The industrial environmental control includes monitoring of specific air contaminants typical of a particular industry. Determination of the pollutant levels at the border of the sanitary protection zone consists of the preliminary sampling and subsequent analysis in a specialized laboratory. The article discusses various methods of sampling for a group of volatile organic compounds (using sample bags) and polyaromatic hydrocarbons (using a sorption tube and a filter to collect solid particles), depending on their physicochemical properties and the characteristics of distribution.

1. Introduction

Enterprises of the mining and metallurgical and petrochemical complex are the sources of emission into the atmosphere of a wide range of pollutants [1]. For each production, its own characteristic substances have been identified, which are included in the program of industrial environmental monitoring (IEM), the purpose of which is to comply with environmental requirements established by law [2, 3]. In the implementation of IEM, it is necessary to take into account the peculiarities of the production process that has a negative impact on the environment, and, in particular, on the ambient air [4]. IEM includes instrumental measurements of pollutant concentrations both at the boundary of the sanitary protection zone (SPZ) and in industrial emissions [5]. Control of industrial emissions, as well as a quality control of the ambient air at the border of the sanitary protection zone, implies periodic sampling at reference points and their further analysis in specialized laboratories. In connection with the adoption of the Federal Law "On Environmental Protection" in 2018, enterprises gradually equip their stationary sources with automated monitoring systems. These systems provide an opportunity to monitor atmospheric releases in real time and see the real picture of pollutant emissions into the atmosphere [6, 7].

It is noteworthy that special attention should be given to volatile organic compounds (VOCs) and polyaromatic hydrocarbons (PAHs) in the matter of industrial environmental monitoring because these substances are markers for many industries and have an adverse impact on human health. Moreover, some of them have carcinogenic properties [8].

2. Results and discussion

The list of VOCs includes more than 150 compounds belonging to different classes of organic substances. Some of them, in addition to irritation, have carcinogenic activity, such as benzene [9]. These compounds have a high vapor pressure at ordinary room temperature and, therefore, they are predominantly present in the ambient air in a gaseous state. Such substances as benzene, toluene, ethylbenzene, xylene isomers are markers for the oil refining industry, they also reach the atmosphere...
during coal mining and enrichment [10]. With reference to the above mentioned, these compounds are included in the IEM program.

Another class of compounds - polyaromatic hydrocarbons (PAHs) - includes several hundred compounds, and only 16 of them were recommended for control by the US Environmental Protection Agency. These compounds are products of incomplete combustion and enter the atmosphere from both natural sources (forest fires, volcanic eruptions) and from anthropogenic (metallurgical industry, petrochemical industry, incineration plants) [11]. The International Agency for Research on Cancer classifies most of these compounds as carcinogens [12]. Unlike VOCs, the saturated vapor pressure of these substances is lower and ranges from $10^{-2}$ to $10^{13}$ kilopascals; therefore, they can be either in the gaseous state or in the solid state in the environment and industrial emissions.

Due to different chemical and physical properties, these compounds require different approaches to their sampling [13]. So, when it is impossible to determine the VOCs concentration in situ, samples of these pollutants should be collected using various devices - sorption and indicator tubes, absorption vessels (for example, Richter, Zaitsev vessels with a porous plate), cooled traps, syringes, gas pipettes and others. Most of these devices have several disadvantages. For example, when using sorption tubes, the concentration of substances in the sample decreases as a result of adsorption by the tube material, while subsequent analysis of the sample on a gas chromatograph may cause false peaks (as a result of desorption of previously adsorbed substances). The use of syringes and gas pipettes does not meet the regulatory and technical documentation for sampling (due to the sampling time), and these devices do not allow storing samples of atmospheric air. Moreover, many sampling devices require considerable time for their cleaning, as well as preliminary preparation of special sorbents and absorption solutions. In this regard, there is a need to introduce new methods and devices for sampling with the aim of determining the concentration of pollutants.

To optimize the quality control of the air environment at the border of the sanitary protection zone, the authors propose to use sample bags, allowing determining the concentration of both priority and marker pollutants. A distinctive feature of these devices is the simplicity of their use, cleaning, transportation, multiple use and the possibility of averaging an air sample over any period of time for further comparison of the analysis result with environmental standards, for example, the maximum one-time maximum allowable concentration [14].

In order to confirm the feasibility and viability of using sample bags, authors conducted an experiment: the concentrations of pollutants were determined in situ (at reference points, without sampling) and in laboratory conditions with preliminary sampling of atmospheric air into the lavsan sample bag. Benzene, toluene, ethylbenzene and xylenes isomers were the subject of the research.

Measurements and sampling of atmospheric air were carried out at two reference points in Kalininisky (point 1) and Kirovskiy (point 2) districts of St. Petersburg. Both points were located on the border of the sanitary protection zone, the size of which, according to Sanitary Rules and Regulations 2.2.1/2.1.1.1200-03, was 50 meters. Measurements and sampling were carried out at 9.00, 11.00, 13.00 and 15.00 o'clock.

Concentrations of pollutants were determined in situ by means of a portable gas chromatograph FGH-1.2 (Research and Production Enterprise “Ekan”, Russia). Sampling in the lavsan sample bags was carried out by the agency of a portable compressor PC-1 (Research and Production Enterprise “Ekan”, Russia). The duration of sampling was 20 minutes.

Measurement of pollutant concentrations in air samples collected in lavsan bags was performed in accredited Environmental Laboratory of the State company "Mineral" according to the "Method for determination of mass concentration of diisobutyl ketone, o-dichlorobenzene, cumene, methylene chloride, perchloroethylene, propyl benzene, styrene, toluene, trichloroethylene, chlorobenzene, vinyl chloride, o-chlorotoluene, cyclopentanone, ethyl acrylate, ethylbenzene, ethyl formate” No.205-28/RA.RU.311787/2016 and “Methods for measuring mass concentration of allyl alcohol, amyl alcohol, acetone, benzene, butyl acetate, butyl alcohol, isobutyl acetate, isoamyl alcohol, isobutyl alcohol, isopropyl alcohol, n-xylene, m-xylene, o-xylene, methyl ethyl ketone, ethylene oxide, propyl alcohol,
cyclohexanone, epichlorohydrin, ethyl acetate" No.01.00225/205-16-13. The results of the experiment are presented in Table 1.

Table 1. The results of determining the concentration of pollutants in atmospheric air, mean value, mg/m³

| VOCs          | Measurement at reference point 1 (in situ) | Preliminary sampling in lavsan bag (point 1) | Measurement at reference point 2 (in situ) | Preliminary sampling in lavsan bag (point 2) |
|---------------|-------------------------------------------|---------------------------------------------|-------------------------------------------|---------------------------------------------|
| Benzene       | 0.002                                     | 0.002                                       | 0.001                                     | 0.001                                       |
| Toluene       | 0.038                                     | 0.036                                       | 0.031                                     | 0.030                                       |
| Ethylbenzene  | <0.001                                    | <0.001                                      | 0.001                                     | <0.001                                      |
| m-Xylene      | 0.066                                     | 0.064                                       | 0.053                                     | 0.051                                       |
| p-Xylene      | 0.053                                     | 0.051                                       | 0.047                                     | 0.045                                       |
| o-Xylene      | 0.017                                     | 0.017                                       | 0.023                                     | 0.022                                       |

Concentrations below 0.001 mg/m³ indicated the presence of a substance (benzene, ethylbenzene) in the sample in an amount less than the threshold of sensitivity of the device. It should also be noted that during the research, the maximum one-time maximum permissible concentrations (MPC) were not exceeded for any pollutant. The minimum and maximum values, mathematical expectation, variance, standard deviation, coefficient of variation were determined.

Based on the results of the experiment, it can be concluded that it is possible and advisable to use lavsan sample bags for the purposes of environmental monitoring of ambient air. This type of device for sampling (together with a compressor or an aspirator), transporting and storing air samples allows obtaining a sample averaged over any time period (for instance, 20 minutes). Sample bags are designed to be repeatedly used provided they are properly cleaned (using zero air or high purity nitrogen).

Unlike VOCs, when monitoring PAHs, it is not enough to analyze only the gas fraction. Sampling should include the collection of the solid component of the gas-air mixture. The separation of PAHs between the gas and solid components will depend on the ambient temperature or the temperature of the technological process, as well as on the total dust content of the gas-air mixture [15]. Examples of the separation of PAHs between phases for atmospheric air and industrial emissions are presented in Table 2.

As the processes occurring in the gas-air mixture in both atmospheric air and industrial emissions are not stable, the sampling of the gas component and the solid one must take place simultaneously under the same conditions. For this purpose, the available measurement methods suggest using a filter for the selection of particles and the sorption tube following it.

Undoubtedly, the PAHs sampling process could be simplified by the use of sample bags with additional filters installed at the bag’s entrance with further analysis by gas chromatography or chromato-mass-spectrometry, but the concentration of these substances in atmospheric air and industrial emissions is much less than the concentration of VOCs. For example, average daily MPC of benzapyrene is $10^6$ mg/m³, and benzene average daily MPC is 0.1 mg/m³, for toluene it is 0.6 mg/m³. So, in the “Methodology for measuring the mass concentration of polycyclic aromatic hydrocarbons in atmospheric air and industrial emissions using high performance liquid chromatography” M-02-902-150-07, it is recommended to collect up to 1000 dm³ of the atmospheric air sample volume.
Table 2. The content of PAH in the gas and solid phases in atmospheric air and industrial emissions, %

| PAHs                       | Temperature -6°C | Industrial emissions | Industrial emissions |
|----------------------------|------------------|----------------------|----------------------|
|                            | gas particles    | gas particles        | gas particles        |
| Naphthalene                | 95.7             | 4.3                  | 86.8                 | 13.2                 | 100 | - |
| 2-methylnaphthalene        | 56.6             | 43.4                 | 87.6                 | 12.4                 | 99.6 | 0.4 |
| Acenaphthene               | 10.2             | 89.8                 | 93.7                 | 6.3                  | 99.5 | 0.5 |
| Fluorene                   | 12.6             | 87.4                 | 91.6                 | 8.4                  | 97.8 | 2.2 |
| Phenanthrene               | 8.7              | 91.3                 | 59.8                 | 40.2                 | 70.9 | 29.1 |
| Anthracene                 | 1.9              | 98.1                 | 87.1                 | 12.9                 | 50.1 | 49.9 |
| Fluoranthenes              | 17.2             | 82.8                 | 7.6                  | 92.4                 | 9.6  | 90.4 |
| Pyrene                     | 9.0              | 91.0                 | 2.1                  | 97.9                 | 5.6  | 94.4 |
| Benzantracene              | 22.3             | 77.7                 | 1.6                  | 98.4                 | 11.3 | 88.7 |
| Chrysene                   | 7.9              | 92.1                 | 1.1                  | 98.9                 | 14.6 | 85.4 |
| Benz(b)fluoranthene        | 4.8              | 95.1                 | -                    | 100                  | 39.9 | 60.1 |
| Benz(k)fluoranthene        | 0.0              | 100                  | -                    | 100                  | 42.2 | 57.8 |
| Benzapyrene                | 0.0              | 100                  | -                    | 100                  | 78.1 | 21.9 |
| Dibenzo(a, h)anthracene    | 39.3             | 60.1                 | -                    | 100                  | 61.1 | 38.9 |
| Benz(g, h, i)pyrene        | 32.1             | 67.4                 | -                    | 100                  | 17.1 | 82.9 |
| Indeno(1,2,3-cd) pyrene     | 43.1             | 56.0                 | -                    | 100                  | -    | 100 |

Such a compound as naphthalene is a site of special scientific interest. Average daily MPC of naphthalene is 0.003 mg/m³. This substance is included in the VOCs list and is also on the list of priority PAHs. As can be seen from Table 2, naphthalene is mainly in the gaseous state in industrial emissions. It can also predominantly be in the gaseous state in atmospheric air, but with decreasing temperature and increasing concentration of suspended particles, the proportion of naphthalene in the solid phase will increase. Sampling methods, developed for the PAHs control, involve the usage of the sorption tube to collect this substance. They are described, for instance, in the measurement method M-02-902-150-07 or in GOST R ISO 11338-1-2008 "Determination of the content of polycyclic aromatic hydrocarbons in the gaseous state and in the form of solid suspended particles". At the same time, according to the certified measurement methods (for example, No.01.00225/205-24-16 “Methods of measuring the mass concentration of aniline, benzaldehyde, butylcarbitol, diisopropyl ether, dimethyl acetamide, isoprene, isophorone, methyl 2-pyrrrolidone, methyl tert-butyl ether, methylcyclohexane, naphthalene, propionic aldehyde, hydrogen sulfide, tetrahydrofuran, toluene, phenol, furfuryl alcohol, furfural, cyclohexanol, ortho-creosol, the sum of meta-creosol and para-creosol in atmospheric air, working zone air, non-productive premises air, industrial emissions by gas chromatography”) sample bags could be used for sampling and subsequent concentration determination of a given substance.

3. Conclusion
The industrial environmental monitoring is an integral part of environmental quality monitoring, and atmospheric air in particular. It is necessary to determine the levels of marker substances both in the industrial emissions and at the border of the sanitary protection zone, taking into account the features of production processes and the physicochemical properties of the compounds. Recently, an increasing number of enterprises use automated systems for monitoring emissions from stationary sources, while measuring concentrations of pollutants at the sanitary protection zone boundary requires preliminary sampling.

Volatile organic compound content monitoring at the boundary of the sanitary protection zone implies periodic preliminary air sampling followed by determination of concentrations in specialized
laboratories. The authors propose the use of lavsan sample bags, which allow one to conduct sampling during any time period, as well as to reuse these devices. The possibility and viability of the use of these bags is confirmed by the research.

When controlling PAHs, both gas and solid components should be collected. In this regard, as well as with the presence of these compounds in atmospheric air in low concentrations, the determination of PAH levels with preliminary sampling cannot be carried out by means of sample bags. For this purpose, the traditional method should be employed - the sampling of air through a sorption tube and a filter to collect particles.

Special attention should be paid to the determination of naphthalene content in the atmospheric air, which is included in both the VOCs and priority PAHs list. According to the methods of PAHs determination, the capture of this substance should be carried out using sorption tubes. However, the existing certified methodologies also allow sampling with the use of sample bags.

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