On comparison of methods for quantitative chemical analysis of atmospheric air

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Abstract. In connection with the increasing anthropogenic load, it is necessary to control the content of various impurities in the atmospheric air. One of these compounds is formaldehyde, which has carcinogenic and mutagenic properties. To measure the concentration of this substance, various methods are used - chromatographic, spectrophotometric, fluorescent. As an alternative to these methods, the authors propose the use of photoacoustic detection. According to the results of comparative tests, this method should be considered suitable for use in monitoring atmospheric air.

1 Introduction

Use 170 x 250 mm paper size (W x H mm) and adjust the margins to those shown in the Table 1. The final printed area will be 130 x 210 mm. Do not add any page numbers Currently, one of the most acute environmental problems is air pollution [1]. The constant increase in anthropogenic load leads to a decrease in the quality of the environment and, as a result, negatively affects the health of the population [1].

According to the chemical composition, properties and nature of the impact on the human body, atmospheric air pollutants can be divided into toxic and non-toxic. Toxic substances include carbon monoxide, nitrogen oxides, a large group of hydrocarbons, aldehydes, soot, and others [1]. One of the toxic specific impurities that have a negative impact on public health is formaldehyde (CH2O).

Anthropogenic sources of CH2O in the ambient air of cities are divided into primary and secondary [2]. The first group includes vehicles emissions, industrial emissions, and coal combustion, the second - the formation of a substance due to photochemical reactions and the processes of transformation of organic compounds (for example, methane, methyl alcohol, formic acid, chlorinated methane) [2]. In some cases, the formation of formaldehyde is facilitated by the presence of high concentrations of nitrogen oxide in the atmosphere, as well as high intensity of solar radiation, which enhances the conversion of hydrocarbons into CH2O [3].

Formaldehyde is toxic, has a mutagenic and carcinogenic effects, negatively affects the central nervous system [4]. The degree and nature of the impact of formaldehyde on a person depends on the concentration of the pollutant, the method of contact (through the

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respiratory system, gastrointestinal tract, skin and mucous membranes) and the individual sensitivity of the organism [4].

The substance is subject to mandatory control in the cities of the Russian Federation with a population of more than 500 thousand inhabitants. In this regard, there is a need for continuous monitoring of the formaldehyde content in the atmospheric air of the residential areas of large cities.

Quantitative determination of formaldehyde in ambient air can be carried out in various ways [1]. In the Russian Federation, for this purpose, as a rule, the methods of chromatography, spectrophotometry, and fluorimetry are used. These methods of analysis have certain advantages and disadvantages, and the choice of method depends on the purpose and objectives of the study, the required accuracy of the measurement results. As an alternative to the above methods for measuring CH2O concentrations, the authors propose to consider photoacoustic detection.

To define the possibility and expediency of using the photoacoustic detection method, the results of measurements of formaldehyde in ambient air, obtained by this method, were compared with the results obtained by means of chromatographic method currently used in the monitoring system of atmospheric air in St. Petersburg.

2 Materials and Methods

During this study, the following equipment and materials were used:

- Gasera ONE Formaldehyde gas analyzer (“Gasera” Ltd., Finland);
- Two-channel portable gas chromatograph FGH-1-2 (Research and Production Enterprise “Ekan”, Russia);
- Thermal diffusion generator of gas mixtures TDG-01 (LLC "Monitoring", Russia);
- Source of microflow IM-GP-94-M-A2 and IM94-M-A2;
- Consumables (PTFE tubes, adapters, carrier gas, etc.).

Additionally, it should be noted that the Gasera ONE Formaldehyde analyzer allows you to receive information about the object of study in real time, automatically selects the amount of sample is needed for analysis and processes the results. When using the FGH-1-2 chromatograph, the measurement is preceded by the procedure for introducing a sample into the device (mechanically), it is also necessary to take into account the longer analysis time and the need for manual processing of the resulting chromatogram by the operator.

To compare the effectiveness of the methods, a research program was compiled, in which the devices simultaneously analyzed the studied air volume (Fig. 1).

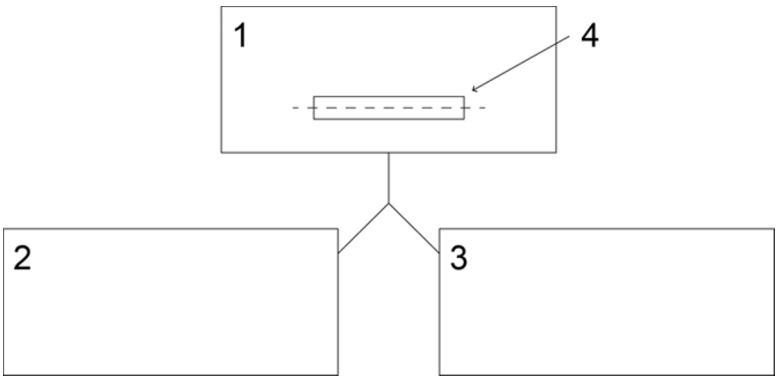

Fig. 1. Equipment connection diagram: 1 - TDG-01; 2 - Gasera ONE Formaldehyde; 3 - FGH-1-2; 4 - Source of microflow

The experiment consisted of the following steps:

1. Check the operability of the equipment, establish the absence of defects.
2. Turn on TDG-01. Equipment warm-up.
3. Set the temperature on TDG-01 according to the technical data sheet of microflow sources (80 °C). Wait for the specified temperature to be reached.
4. Set on TDG-01 the air flow required for the correct operation of microflow sources (2000 cm3/min).
5. Switch on the measuring devices FGH-1-2 and Gasera ONE Formaldehyde. Equipment warm-up. Carry out the necessary procedures according to the measurement procedures.
6. Connect measuring devices to TDG-01: connect the tube at one end to the outlet of TDG-01, install an adapter connector at the other end of the tube and then connect each branch tube to the corresponding device.
7. Place the microflow source in TDG-01 (IM-GP-94-M-A2).
8. Carry out analysis according to measurement procedures.
9. Replace the microflow source (IM94-M-A2).
10. Carry out analysis according to measurement procedures.
11. Place in TDG-01 two sources of microflows simultaneously.
12. Carry out analysis according to measurement procedures.
13. Switch off the equipment according to the technical documentation.
14. Processing and analysis of the received data.

In total, two series of tests were carried out with each of the microflow sources, as well as with their joint use. Each series had 8 measurements with Gasera ONE Formaldehyde and 2 measurements with FGH-1-2. The number of obtained measurements in each series was related to the duration of the analysis by different methods.

In the course of processing the results, the average values of each series of measurements were determined, standard deviations and measurement errors were found for each method.

3 Results and discussion

The results of the experiment are presented in Table 1.

Table 1. Results of formaldehyde concentration measurements by chromatographic and photoacoustic methods.

Gasera ONE Formldehyde						
Measurement No.	Formaldehyde concentration, mg/m3					
	IM-GP-94-M-A2		IM94-M-A2		IM94-M-A2 and IM-GP-94-M-A2	
	Series 1	Series 2	Series 3	Series 4	Series 5	Series 6
1	0.0491	0.0485	0.0707	0.0707	0.1209	0.1209
2	0.0497	0.0500	0.0725	0.0706	0.1203	0.1195
3	0.0499	0.0503	0.0717	0.0710	0.1206	0.1202
4	0.0484	0.0516	0.0730	0.0713	0.1204	0.1204

5	0.0467	0.0507	0.0727	0.0718	0.1195	0.1202
6	0.0483	0.0485	0.0737	0.0725	0.1197	0.1201
7	0.0489	0.0498	0.0735	0.0728	0.1204	0.1185
8	0.0483	0.0507	0.0725	0.0725	0.1209	0.1195
FGH-1-2						
Measurement No.	Formaldehyde concentration, mg/m3					
	IM-GP-94-M-A2		IM94-M-A2		IM94-M-A2 and IM-GP-94-M-A2	
	Series 1	Series 2	Series 3	Series 4	Series 5	Series 6
1	0.0455	0.0486	0.0704	0.0705	0.1193	0.1204
2	0.0483	0.0492	0.0694	0.0696	0.1184	0.1186

According to the data obtained, a statistical analysis was carried out, during which the errors of the methods were established. Table 2 shows the calculated errors of each series of experiments for each method relative to the target concentration of formaldehyde.

Table 2. Calculated errors of photoacoustic detection and chromatographic methods of analysis.

Series No.	Photoacoustic detection method	Chromatographic method
1	7,6 %	11,5 %
2	4,1 %	7,6 %
3	6,5 %	7,8 %
4	5,2 %	7,8 %
5	3,2 %	4,8 %
6	4,0 %	4,1 %

Based on the results of the experiment, it can be concluded that both measuring devices showed satisfactory results and correspond to the declared metrological characteristics (the limits of the reduced / relative error in measuring the mass concentration of formaldehyde are ±20 % for Gasera ONE Formaldehyde and ±25 % for FGH-1-2). At the same time, Gasera ONE Formaldehyde showed values closer to the target ones, what indicates the suitability of this device and the method of photoacoustic detection for ambient air monitoring.

4 Conclusion

The increasing anthropogenic load on the environment requires the introduction of new methods and techniques of ambient air monitoring. There are a number of methods by which it is possible to determine the content of formaldehyde in the air. Among them, for the purposes of monitoring, the method of chromatographic analysis is widely used. It has both obvious advantages and a number of disadvantages, including the complicated introduction of a sample into the device or the need for a sampling and sample preparation procedure, a long analysis time, and processing of chromatograms with the help of an operator. As an alternative to this method, the authors propose photoacoustic detection. An experiment was carried out to define the possibility and expediency of using this method for ambient air monitoring. During the study, it was found that the equipment used (portable chromatograph FGH-1-2 and gas analyzer Gasera ONE Formaldehyde) corresponds to the declared metrological characteristics. At the same time, according to the results of all series of the experiment, the device, the principle of which is based on the photoacoustic method of analysis, showed values closer to the target ones. On this basis it can be concluded that this measuring device could be implemented into the ambient air monitoring system. Moreover, it is worth noting the simplicity of its operation and the automated process of obtaining measurement results.

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