DEVELOPMENT OF A METHOD TO DETERMINE CONCENTRATIONS OF ORGANIC COMPOUNDS (ETHYLENE OXIDE, 1,3-BUTADIENE, ACRYLONITRILE) IN AMBIENT AIR AT REFERENCE LEVELS [1]

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Abstract. The paper presents the results of experimental studies on the development of gas chromatographic methods for the identification of 1,3-butadiene and ethylene oxide, acrylonitrile in ambient air at reference concentrations. The sorption of the studied compounds from the air on Tenax TA sorbent in combination with the optimal conditions for the thermal desorption and capillary gas chromatography were used The parameters of adsorption, desorption and gas chromatographic determination of 1,3-butadiene and ethylene oxide, acrylonitrile, in the atmospheric air are determined. Achieved high sensitivity gas chromatographic determination in the range of concentrations (mg/m3): 1,3-butadiene 0.002–5.0, ethylene oxide, 0.005–1.0, acrylonitrile 0.002–1.0 mkg/sm3 methods to determine whether the error exceeds 25 % .
Keywords: reference concentration (RfC), 1,3-butadiene, ethylene oxide, capillary gas chromatography, flame ionization detector, thermionic detector, thermal desorption, internal quality control, chemical analysis

Introduction. Exposure assessment methodology is based on the research methods that include the measurement of chemical compounds concentrations in the environment for a more precise determination of the real levels of impact of chemical exposure on human health [1]. Qualitative characteristics of exposure include determination of the concentrations of chemical compounds that affect human health during the exposure period including low chemical compound concentrations in chronic daily intake at the reference level. Such tasks demand stricter requirements for the instrumental control of the environment for the purpose of obtaining credible information about public exposure and environmental pollution. The requirements include, among others, an increase of the test method sensitivity to the reference concentration levels (RfC) for the determination of chemical compounds in ambient air and risks associated with public health. In order to conduct the studies at such level of concentrations, it is necessary to develop essentially new methods of analysis.

Human exposure to environmental pollution can result in the development of various effects depending on the length, volume and frequency of exposure. 1,3-butadiene and ethylene oxide, acrylonitrile are known to be highly toxic substances (hazard category 2 and 3), and according to LARC (Agency for Research on Cancer), ethylene oxide is a group 1 carcinogen, and 1,3-butadiene and acrylonitrile are group 2A carcinogens [2]. The general toxic effect of ethylene oxide consists of changes in the lymphatic system and blood circulatory system (lymphocytic leukemia and non-hodgkin lymphoma) [3]. 1,3-butadiene can cause leukemia; acrylonitrile can contribute to the development of central nervous system tumors [4]. The presence of these compounds in the environment can have an adverse effect on public health [5].

The methods of environmental analysis described in the guidance documents provide for the determination of the studied compounds in ambient air in the following span of

[1] *Translated by Ksenya Zemnlyanova*

concentrations: ethylene oxide – from 0.3 to 6 mg/m3 2[6], 1,3-butadiene – 1–1500 mg/m3 3[7], acrylonitrile – 0.01 – 1.0 mg/m34 [8]. Such level of sensitivity does not suffice for an adequate risk assessment. The above factors determine the urgency of these studies and help identify the purpose of the work – to develop highly sensitive and selective methods for the identification of 1,3-butadiene, ethylene oxide and acrylonitrile in ambient air at the levels that correlate with the permissible risk levels of concentrations to public health.

Materials and research methods. The research was conducted by the specialists of the chemical and analytical department of the Federal Scientific Center for Medical and Preventive Health Risk Management Technologies. The objects of the research included ambient air, gas chromatographic methods development procedures: sorption environments, chromatographic behavior of the studied compounds at various stationary liquid phases, metrological characteristics of the measurement process, and ambient air sample collection methods. Ambient air was studied using the method of capillary gas chromatography with various types of detectors (1,3-butadiene, ethylene oxide, acrylonitrile). The samples of organic compounds in ambient air were collected on sorbent tubes followed by thermal desorption and analysis on gas chromatograph Crystal-5000 that uses PoraPlot Q -25m•0.53mm•0.5µm capillary columns. In order to build a calibration chart, a series of standard gas mixtures of 1,3-butadiene and ethylene oxide were prepared in nitrogen of various concentrations with the use of Microgas-F dynamic station.

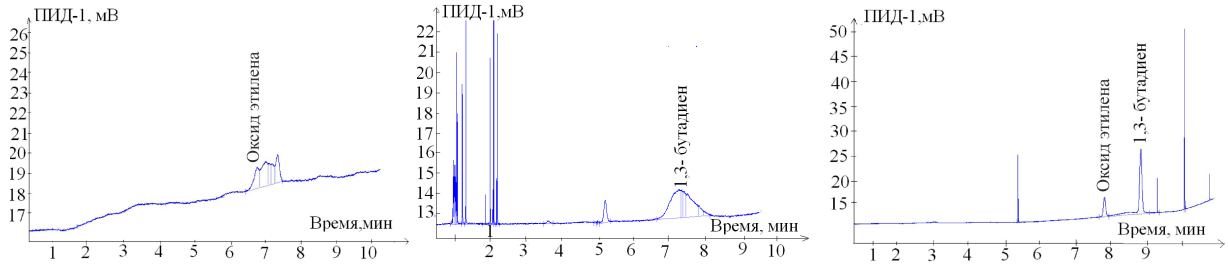
The development of methods for the identification of 1,3-butadiene, ethylene oxide and acrylonitrile in ambient air was based on the following principles: determination of chromatographic behavior of the substances in conditions of analysis (separation criteria); selection of optimum conditions for the sample preparation (sorption) and quantitative measurement; study of the recovery rate by the use of 'input-output' method; development of effective methods and tools for the collection of ambient air samples; determination of metrological characteristics of the measurement process.

Results and discussion. 1,3-butadiene and ethylene oxide. We studied the separation conditions on the capillary columns with various characteristics of stationary liquid phases – Optima-5-25m•0,32mm•5.0µm, HP-FFAP-50m•0.32mm•0.5µm, GasPro-25m•0.32mm•0.5µm and PoraPlot Q -25m•0.53mm•0.5µm. The chromatograms of standard mixtures of 1,3-butadiene and ethylene oxide are presented in Figure 1.

Optimum temperature of the gas chromatography analysis was determined by adjustment guided by the boiling temperatures and volatility of the studied compounds and parameters of the

[2] Methodological Guidelines MUK 4.1.1299-03 Gas chromatography assessment of mass concentrations of acetaldehyde, oxirane (ethylene oxide) in workplace air, Adopted 30 March, 2003.
[3] PND F 13.1.:2:3.23-98. Methodology for the assessment of saturated hydrocarbons C_1-C_5 and unsaturated hydrocarbons (ethane, propene, butane) in ambient air, workplace air and industrial emissions by the use of gas chromatography, Moscow, 1998.
[4] MUK 4.1.1044a-01. Gas chromatographic assessment of acrylonitrile, acetonitrile, dimethylamine, dimethyl formamide, diethyl amine, propylamine, and triethylamine ethylamine in ambient air. Volume 2, Russia's Ministry of Health. Moscow. 2002.

capillary column sorbents. Gas chromatography parameters for the identification of 1,3-butadiene and ethylene oxide in the samples of standard gas mixtures are presented in Table 1.



a *b* *c*

a – PID-1, mV
Ethylene oxide
time, min

PID-1, mV
Ethylene oxide
time, min

PID-1, mV
Ethylene oxide
1,3-butadiene
Time, min

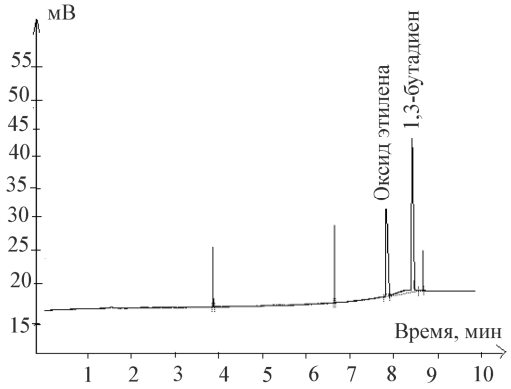
Figure 1. The chromatograms of the standard gas mixture of 1,3-butadiene and ethylene oxide obtained on the capillary columns with various stationary luquid phases: a)- column Optima-5-25m•0.32mm•5.0µm, б)- column GasPro-25m•0.32mm•0.5µm, в)- column PoraPlot Q -25m•0.53mm•0.5µm. Full separation of the standard gas mixtures of 1,3-butadiene and ethylene oxide with other hydrocarbons the following was obtained on the capillary columns PoraPlot Q -25m•0.53mm•0.5µm.

Table 1

Gas chromatography parameters for efficient separation of the gas mixture of 1,3-butadiene and ethylene oxide

Mode	Temperature, ^{0}C		Carrier gas flow rate, ml/min
	column	Heating rate, ^{0}C/min	
1	70^{o}C–120 ^{o}C–140	8 –5	20
2	70^{o}C–120 ^{o}C–140	15–5	30
3	70^{o}C–120 ^{o}C–140	10 –5 (including initial cooling at 50 ^{o}C)	14,1

Complete separation was obtained in mode 3 which was selected for further studies. A chromatogram of a standard gas mixture of 1,3-butadiene and ethylene oxide with characteristic parameters is presented in Figure 2.



mV
Ethylene oxide
1,3-butadiene
Time, min

Figure 2. Chromatogram of a standard gas mixture of 1,3-butadiene (c=0.004 mg/m^3) and ethylene oxide (0.00116 mg/m^3)

Qualitative identification of 1,3-butadiene and ethylene oxide was conducted with the method of absolute calibration using six series of standard gas mixtures in the span of concentrations for 1,3-butadiene 0.002 – 5.0, ethylene oxide – 0.005 – 1.0 mg/m3. A calibrating characteristic was considered stable in case of fulfillment of the following condition:

$|X - a| \le K_{cp}$, where

a – standardized sample value for calibration;

X – results of the measurement of weight concentration of 1,3-butadiene and ethylene oxide in calibration samples;

Kcal – stability control specification for the calibrating characteristic

We analyzed the efficiency of thermal desorption of ethylene oxide and 1,3-butadiene by using several sorbents. The following sorbents were used in the studies: molecular sieves, chromosorb106, Spherocarb TM, Carbopack/Carbosieve S-III/Carboxen 1000, Tenax TA. Mean values of the thermal desorption rates of the analyzed compounds from the sorbents are presented in Table 2.

Table 2

Mean values of the completeness of sorption of 1,3-butadiene and ethylene oxide

Sorbent	1,3-Butadiene			Ethylene Oxide		
	Concentration, mg/m^3					
	Input	Output	Desorption rate, %	Input	Output	Desorption rate, %
1. Molecular sieves	1.00	0.892	90	0.50	0.425	85
2. Chromosorb 106	1.00	0.836	85	0.50	0.403	80
3. Spherocarb TM	1.00	0.945	95	0.50	0.454	90
4. Three-layer sorbent Carbopack/Carbosieve S-III/Carboxen 1000	1.00	0.970	97	0.5	0.475	95
5. Tenax TA	1.00	0.985	98.5	0.5	0.485	97

Our studies show that Tenax TA polysorbent has the most optimum characteristics. The highest rate of thermal desorption is 98.5 % for 1,3-butadiene, and 97 % for ethylene oxide.

The newly developed method is based on preliminary collection of 1,3-butadiene and ethylene oxide from ambient air on the sorption tube filled with Tenax TA sorbent, thermal desorption followed by gas chromatography analysis and the application of flame ionization detector. The obtained levels of detection in ambient air were as follows (mg/m3): 1,3-butadiene – 0.002, ethylene oxide – 0.005. Metrological certification [10] of the developed method can be used for the identification of the values of the indicators of the measurement results acceptability: accuracy ±25 %, reproducibility limit for 1,3-butadiene – 9.76 %, ethylene oxide – 4 %.

Acrylonitrile. Gas chromatography parameters for the identification of acrylonitrile in ambient air are presented in Table 3.

Table 3

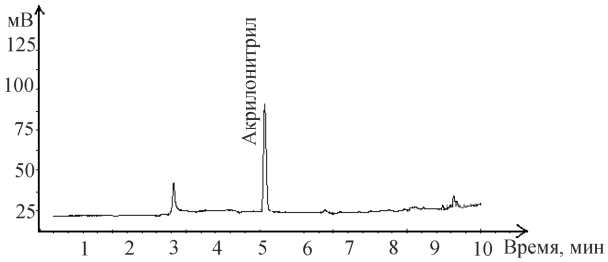
Gas chromatography parameters for the identification of acrylonitrile in ambient air

Mode	Temperature, ^{0}C		Carrier gas flow, ml/min	Flow ratio nitrogen:air
	column	Heating rate, ^{0}C/min		
1	50–200	10	20	1:14
2	70–160–180	15	30	1:20
3	70–160–200	25	30	1:0

Complete separation of acrylonitrile and other hydrocarbons was obtained in mode 1.

The method of determination of acrylonitrile in ambient air is based on the collection of the analyzed compound from air on the sorption tube filled with Tenax TA sorbent, then thermal desorption followed by gas chromatography analysis on the capillary column DB-624-30m*0,32mm*1.8μm with the use of thermionic detector. For qualitative determination of acrylonitrile, we identified a calibration characteristic by the method of absolute calibration in six series of standard mixtures in the span of concentrations 0.002–1.0 mcg/cm3. To do that, we introduced 1 mm3 of one of the calibration mixtures through a small opening in the sorption tube onto the sorbent at 5-8 mm deep. The sorption tube was placed into a device for thermal desorption where the tube was heated for the purpose of desorption of acrylonitrile vapor in the flow of the carrier gas. For optimum effectiveness of desorption, the volume of the gas flow through the tube was 30 to 50 cm3/min.

Conditions for desorption of analyte from the sorption tube with a sample: *preparation* (initial): temperature of the tube – 0 ^{o}C, temperature of the trap – 20 ^{o}C, flow of the carrier gas 10 ml/min, stabilization time – 0:00:30 min; *desorption*: temperature of the tube – - 200 ^{o}C, flow of the blow-down gas – 40ml/min, desorption time – 0:07:00 min; *analysis*: temperature of the trap (high) – 200 ^{o}C, heating rate – - 2000 ^{o}C/min; heating time – - 0:02:00 min; *cleaning of the tube*: temperature of the tube–250 ^{o}C, flow of the blow–down gas–50 ml/min, sorbent used on the Tenax TA trap – 40–100 mg. Chromatogram of a standard acrylonitrile solution obtained in the above conditions is presented in Figure 2.



Легенда
mV
Acrylonitrile
Time, min

Figure 3. Chromatogram of a standard acrylonitrile solution (C_{AN}=0.0029 mcg/cm^3)

The analysis of the completeness of sorption of acrylonitrile vapor by various solid sorbents (molecular sieves, Chromosorb106, Spherocarb TM, Tenax, Porapak N, three-layer sorbent Carbopack/Carbosieve S-III/Carboxen) was conducted with the use of the "input-output" method. The analysis showed that Tenax TA sorbent has the optimum characteristics with 96.7

% desorption level. The average value of the completeness of desorption of the studied compound with the sorbent are presented in Table 4.

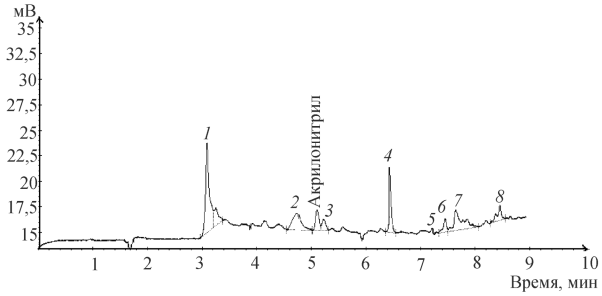
Table 4

Average value of the completeness of sorption of acrylonitrile

Sorbent	Input, mcg	Output, mcg	Level of Desoprtion, %
1	2	3	4
1. Molecular sieve	0.00150	0.00135	90.0
2. Chromosorb 106	0.00150	0.00128	85.0
3. Sherocarb TM	0.00150	0.00142	95.0
4. Carbopack/Carbosieve S- III/Carboxen	0.00150	0.00143	95.6
5. Porapak N	0.00150	0.00144	96.0
6. Tenax TA	0.00150	0.00145	96.7

Evaluation of the method helped us determine metrological characteristics: precision limit – 12 %, reproducibility limit – 14 %, accuracy factor ± 24.85 %.

Testing of the new method was conducted in the form of analysis of the quality of ambient air in the area with chemical, oil and gas, fuel, and electric engineering enterprises the emissions of which contain common and industry-specific pollutants including acrylonitrile. Chromatogram of ambient air samples from a heavily industrialized area is presented in Figure 3.



Легенда
mV
Acrylonitrile
Time, min

Figure 4. Chromatogram of ambient air samples containing acrylonitrile (C_{AN}=0.0022 mcg/m^3) and collected in a sanitary protection zone in the location of chemical enterprises. 1, 2, 3, 4, 5, 6, 7, 8 – unidentified peaks that are of no interest for the purpose of the study

The analysis determined the presences of acrylonitrile in ambient air in a concentration span of 0.002 – 0.0024 mg/m3.

Conclusions. The newly developed gas chromatography method for the identification of 1,3-butadiene and ethylene oxide allows for the identification of the analyzed compounds in ambient air in the presence of other hydrocarbons at the level of reference concentrations. High sensitivity of gas chromatography identification of 1,3-butadiene and ethylene oxide in the span of concentrations (mg/m3): 1,3-butadiene 0.002 – 5.0, ethylene oxide 0.005 – 1.0 with the identification method error of 25 % was obtained by sorption of the analyzed compounds from ambient air on Tenax TA sorbent combined with optimum conditions of the sample preparation and the use of capillary gas-liquid chromatography. A new method for the identification of

acrylonitrile in ambient air was developed and evaluated based on sorption of acrylonitrile from ambient air on Tenax TA sorbent combined with optimum conditions of the sample preparation, thermal desorption and the use of capillary gas-liquid chromatography. The method can be used for the identification of acrylonitrile in air samples at the level of reference concentration 0.002 mg/m3 with a recovery rate of 96.7 % and maximum error of 25 %.

It is recommended to use the new methods to measure mass concentrations of 1,3-budatiened, ethylene oxide and acrylonitrile in ambient air at the level of reference concentrations when conducting risk assessment studies.

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