ABSTRACT

of the thesis for the degree of Doctor of Philosophy (Ph.D.) on educational program «8D05301 – Chemistry»

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Development of simple and accurate methods for organic pollutants determination in the air based on solid-phase microextraction

Characterization of the work

This study is aimed at the development of low-cost, accurate, "green" and simple methods for the determination of the single and time-weighted average (TWA) concentrations of volatile organic compounds (VOCs) in air based on solid-phase microextraction (SPME). Also, this study is devoted to the approbation of the developed methods for determination of VOCs in ambient air.

The relevance of the work

Air pollution is a serious global problem affecting human health and the environment. According to World Health Organization (WHO), in 2019, 99% of the world breathed air, the quality of which was below WHO's limits. Air pollution is caused by various sources, including industrial emissions, coal/biofuel combustion, transportation, and agriculture. Long-term exposure to air pollution can lead to a range of health problems including lung cancer, heart disease, and respiratory illnesses. Moreover, the direct impact of air pollution on increase of COVID-19 cases has been established. Air is one of the most complex environmental objects for the analysis. There are many drawbacks associated with the sampling, sample preparation, and transportation of air samples. Air pollutants can be divided into two main groups: inorganic, which include particulate matter, NO_x, SO_2, CO, ozone, heavy metals, etc., and organic pollutants, which include semi-volatile and volatile organic compounds. VOCs are a group of chemicals that can evaporate from various sources, such as solid fuel combustion, vehicle emissions, industrial activities, biogenic sources, etc. Some of VOCs can have hazard effects on human health, also VOCs can contribute to formation of secondary aerosols and ground-level ozone.

Conventional methods for the determination of organic pollutants are based on sampling on sorbent tubes or in special canisters. The use of special canisters and sorbent tubes requires preliminary cleaning from possible contaminants with high-purity gases before sampling. In addition, deactivation of the inner part of the samplers is needed to prevent analytes adsorption. For analytes desorption from sorbent tubes, expensive thermal desorption equipment or toxic solvents for chemical desorption are required. To improve separation and increase the accuracy of sample analysis, cryogenic focusing of all analytes in the inlet or column of the GC must be used. These drawbacks limit the application of standard methods in developing countries. In Kazakhstan, monitoring of organic pollutants concentrations in the air has not been carried out due to these limitations. To solve these problems, the development of cost-effective, simple, and accurate methods for the determination organic pollutants in the air are required.

The most promising method for the determination of VOCs in ambient air is SPME, which excludes the drawbacks of conventional methods. SPME combines sampling and sample preparation in a single step and meets the principles of "green" analytical chemistry. SPME is based on the sorption of VOCs by a micropolymeric coating followed by the desorption of analytes directly in the GC inlet. SPME can be used to determine single and time-weighted average VOC concentrations. SPME is the simplest sampling method for determining of VOC concentrations in air. However, there are limitations to using SPME-based methods for air analysis, such as complex calibration, losses during storage and transportation, and the main disadvantages are low accuracy and precision. Thus, the development of methods based on SPME, which can improve the existing drawbacks for the determination of single and TWA concentrations of VOCs in the air is still an important task.

The aim of the study: development of simple and accurate methods based on solid-phase microextraction, which can improve the current methods, for the determination of single and time-weighted average concentrations of organic pollutants in the air.

The tasks of the study:

1) To develop a low-cost and accurate method for the determination of single concentrations of more than 20 VOCs in ambient air;
2) Application of the developed method for the assessment of seasonal variation and spatial distribution of VOCs and identification of their possible sources in the air of Almaty;
3) To assess the effect of COVID-19 restrictions measures on air quality in Almaty associated with organic pollutants;
4) To develop a model for SPME extraction for the determination of TWA concentrations of VOCs using finite element analysis-based model;
5) To prove that the developed model can be used for the development of an accurate method for quantification of VOCs TWA concentrations in the field using SPME.

Objects of the study: methods for quantification of multiple volatile organic compounds in air using solid-phase microextraction.

The subjects of the research: accuracy and simplicity of methods for determination of VOCs in the air; single and TWA concentrations of VOCs in the air of Almaty.

The methods of the research

To achieve the aim and solve tasks of the research complex modern physicochemical research methods were used. The following methods were used in this work: solid-phase microextraction in combination with gas chromatography and mass spectrometric detection (GC-MS) for the analysis of air samples; scientific method for the formulation of hypotheses and design of experiments.

The scientific novelty of the research

1) A new method for the quantitation of more than 20 VOCs single concentrations based on sampling into 20 mL vials and analysis by SPME GC-MS was developed.
2) Seasonal and spatial variations of organic pollutants in the ambient air of Almaty were evaluated for the first time.

3) For the first time, the effect of the COVID-19 lockdown measures on the concentrations of organic pollutants in Almaty air was studied.

4) A model for SPME extraction of VOCs by fiber coating located inside the protecting needle was developed using finite element analysis software. The sampler with an alternative geometry was proposed to increase the accuracy of the determination of TWA concentrations of VOCs.

5) A new method for the determination of TWA concentrations of VOCs in ambient air using sampler with alternative geometry and SPME fiber was developed for the first time.

The validity and reliability of the results

The obtained results were valid and reliable since all experiments were carried out with one or two independent variables, while the rest of the variables were constant. The dependent variables displayed the main parameters of the methods, such as the accuracy, recovery, analyte responses, limits of detection and quantification, and reproducibility. All measurements were conducted in two – four replicates. Gas chromatography with mass spectrometric detection was used to achieve the sensitive and selective identification and separation of VOCs.

The theoretical and practical significance of the thesis

The theoretical significance of the work is based in the development of simple and accurate methods for the determination of multiple organic pollutants in the air. Also, the theory of the determination of time-weighted average concentrations by solid-phase microextraction was improved. The proposed sampler with alternative geometry was used for improving the accuracy of the determination of TWA concentrations by SPME.

The developed methods for the determination of single and TWA concentrations of multiple volatile organic compounds in the air can be used by the environmental laboratories to conduct monitoring. The results of the investigation of seasonal and spatial variations of organic pollutants in the air of Almaty can be used by decision makers to develop activities for air quality improvement.

The main provisions to be defended

1) The 65-μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) SPME fiber provides a better combination of detection limits (from 0.010 to 7 $\mu g/m^3$) and relative standard deviations (RSDs) of slopes (<10% for 22 analytes) compared to 85-μm Carboxen (Car)/PDMS, 100-μm PDMS and 50/30-μm DVB/Car/PDMS for the determination of 25 volatile organic compounds in the air.

2) The developed method based on SPME with a 65-μm PDMS/DVB coating provides spike recoveries in the range from 90 to 105% for 20 out of 25 studied analytes.

3) The seasonal variations of 9 out of 19 studied VOCs were significant ($p< 0.01$) with maximum concentrations on winter sampling days in Almaty in 2020.

4) Decreasing diameter of the diffusion path from 0.75 to 0.34 mm allows achieving better accuracy of the determination of TWA concentrations of 9 out of 13 VOCs using Car/PDMS SPME fiber exposed in a glass liner.

The main results of the study:

1) The 65 μm PDMS/DVB fiber provides a better combination of LODs and RSDs of slopes for the simultaneous determination of single concentrations of 25 VOCs. The LODs for 25 VOCs varied from 0.010 to 7 μg/m^3, and the RSDs were low 10% for 22 out of 25 VOCs. The RSDs for methyl ethyl ketone, 1,2-dichloroethane, and *p*-xylene were 25, 20 and 15%, respectively.

2) The effects of the extraction, desorption and storage times were investigated. According to the obtained results, the extraction time of 10 min and desorption time of 1 min were chosen as optimal. To achieve the highest accuracy of the developed method, samples should be analyzed during the first 8 h after sampling.

3) The developed method for the determination of single VOC concentrations provides spike recoveries of 90–105% for all analytes, except methyl ethyl ketone, methylene chloride, 3-picoline, and *n*-hexadecane. Ambient air in Almaty was monitored using the developed method. Mean concentrations of 23 out of 25 VOCs, except methyl ethyl ketone and 1,2-dichloroethane, were 0.2 – 83, 0.1 –70 and 0.1 – 74 μg/m^3 on 30 March, 2 and 4 April 2019, respectively.

4) The developed method of simultaneous determination of single concentrations of 25 VOCs was used for the first time to study the seasonal variation and spatial distribution of the total VOCs in the air of Almaty in 2020. Significant seasonal variations were observed for 9 out of 19 VOCs with maximum concentrations in the winter sampling days, which can be associated with higher emissions from coal combustion, environmental conditions, and geographic location of the city. The total VOCs were 233 – 420, 231 – 437, 48 – 151, 46 – 133, and 72 – 393 μg/m^3 on the sampling days in January, April, April-May, July, and October, respectively. The spatial distribution of TVOCs was similar in all studied seasons, with lower concentrations in the south and higher concentrations in the north of Almaty, where CHPs are located.

5) The comparison of heating and non-heating periods and analysis of typical BTEX ratios showed that air pollution in Almaty has a complex nature with two main sources: burning of biomass/biofuel/coal and vehicle emissions. Solid fuel combustion had a dominant effect on air pollution during the heating season in Almaty, especially coal combustion by CHPs and private houses. In addition, it was found that the sampling sites were mostly affected by aged air masses from remote sources.

6) The effect of COVID-19 lockdown measures (traffic-free conditions) in 2020 on improving air quality in Almaty was studied by comparing the BTEX concentrations during the lockdown period with the same periods in previous years (2015-2019) to exclude the influence of meteorological parameters. The average concentrations of benzene and toluene were 3- and 2-times higher during the lockdown period, respectively, which indicates that the sources of these compounds were active during the lockdown and could be associated with coal combustion by power plants and households. The average concentrations of ethylbenzene and *o*-xylene were 4 and 2.7 times lower, respectively, in 2020 than during the same sampling period in 2015-2019.

7) The simulation of TWA air sampling by retracted SPME fiber using a finite element analysis-based model (using COMSOL Multiphysics software) decreases the

time and cost of experiments for method optimization and/or development, decreases the uncertainty, and helps understand the extraction processes more deeply.

8) The proposed sampler with an alternative geometry allows to increases the accuracy of the determination of TWA concentrations of VOCs in ambient air in comparison with the SPME GC liner. The developed method based on a sampler with an alternative geometry and 85 μm Car/PDMS SPME fiber provides greater recoveries at Z=67 mm for 9 out of the 12 studied VOCs. The developed method in dynamic mode showed substantial similarity to the sorbent tube-based method, except for 1,2-dichloroethane and naphthalene.

Relation of the thesis with research and government programs

This research work was conducted within the framework of projects funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan: Grant No. AP05133158 “Development of analytical methods, materials and equipment for cost-efficient “green” environmental monitoring” (2018-2020 yy.) and Grant No. AP09058606 “ Development of method for determination of organic pollutants time-weighted average concentrations for monitoring of ambient air of Almaty” (2021-2023 yy.).

The author's contribution to this research work consists in the literature review under the topic of the thesis, formulation of scientific questions and hypotheses, planning and conducting experiments, statistical evaluation of the obtained data and writing reports and articles based on the final results.

Publications

The main results of this research work were published in scientific papers, including:

– 4 articles in international journals with impact factors 3.11, 10.754, 3.344, and 4.927, indexed in Web of Science and/or Scopus databases;

– 1 article in the journal recommended by the Committee for Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;

– 2 patents for invention;

– 2 abstracts at international conferences and congress, including 1 abstract at foreign international conference (United states of America (USA)).

The structure of the thesis. The thesis is presented in 110 pages and contains 25 tables, 42 figures, and 161 references. The thesis consists of introduction, six sections, conclusion, list of references, and annex.