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SCREENING OF VOLATILE ORGANIC POLLUTANTS IN WATER OF ALMATY LAKE-SETTLER BY SPME-GC-MS

Abstract: Environmental problems of big cities are directly related to the high concentration of population, industry and transport in small areas, which are the cause of a large number of industrial and domestic emissions. These emissions may represent a different kind of chemical compounds: volatile, semi-volatile and toxic organic compounds, which can be merged with water and pollute it. As a result there are several so-called lake-settlers, where contaminated water is stored for further purification. An annual monitoring of these lakes it is necessary carry out for to prevent the possibility of getting these compounds in drinking water and harm to the environment. The Environmental Protection Agency offered EPA 8270S method for determination volatile and semi-volatile compounds in the environmental objects by GC-MS. However, this technique is not economically profitable, since it requires the use of expensive reference materials for calibration curve and set retention times of all 210 compounds and organic solvents for extraction. The aim of this work is to develop a new selective, informative and efficient green method for the detection of VOCs in water without using organic solvents for extraction and without require of use expensive standard samples. Method of solid phase microextraction and GC/MS with identification of peaks by Kovatc's indices is the most appropriate responding to all requests for the detection of VOCs in the environment. The green method will enable to determine VOCs in environmental objects. Results of work included the optimization of SPME parameters and calculation of retention times of n-alkanes. Using the retention times and retention indices of n-alkanes the dependence was built, which allowed to calculate the retention times of 210 organic pollutants. Also this method was successfully applied for analysis of water from Almaty Lake-Settler «Sorbulak» and 68 main organic compounds were identified, including phenolic compounds, pesticides and polyaromatic hydrocarbons.

Key words: Volatile organic compounds, Kovacs indices, Solid-phase microextraction, Gas chromatography, Mass spectrometry.

1 Introduction

Volatile Organic Compounds (VOCs) are carbon-containing compounds that evaporate easily from water to air at normal room temperatures. VOCs are contained in a wide variety of commercial, industrial and residential products including fuel oils, gasoline, cleaners and degreasers, paints and pesticides [1]. VOCs are one of the main problems in the environment and their wide distribution has raised major concerns, in particular with environmental sciences. The main subgroups of VOCs include halogenated organics, monocyclic aromatic hydrocarbons, organic sulfides and sulfoxides, BTEX, acetone, and esters. VOCs may be of biogenic or anthropogenic origin. Major anthropogenic sources of VOCs to the aquatic environment are paints and coatings, gasoline, solvents, industrial and urban wastewaters, urban and rural run-offs, and atmospheric depositions [2]. The analysis of VOCs is of growing interest due to their impact on global environmental conditions and human health. Of total dissolved organic carbon, 10% is VOCs in relatively unpolluted waters and the concentrations are much higher in raw waters from different anthropogenic sources [3]. Further, for halogenated VOCs, the substitution of halogens is known to affect the chemical and toxicological properties in water. Hence, to get deep insight into the occurrence of

VOCs, analytical techniques at environmental become crucial. Analysis of environmental waters is not a simple issue, not only because of the diversity of analytes and the range of their available concentrations but also due to the complexity of the matrix in which they are present. Therefore, choosing appropriate methods of analysis, determination and identification need to depend on selective, sensitive and cost beneficial. The most efficient technique for determining and understanding the occurrence of VOCs in environmental objects is gas chromatography (GC) [4]. In the majority GC apparatus performance in the determination VOCs carry out with combining classical detectors, such as flame-ionization detector, electron-capture detector, and photo-ionization detector. The most popular detector is mass-selective detector, which has been widely accepted for separation, identification and quantification of VOCs at ng/L or mg/L levels [5-8]. Sample preparation is the most important step of VOC's determination in water samples by chromatographic analysis. The sensitivity of the detector used, appropriate sample preparation and pre-concentration methods applied become significant for the trace determination of VOC's. One of the frequently used methods for sample preparation is Purge and trap technique (P&T) [9-13]. Apart from sensitivity, P&T has the advantages of precision and possibility of automation. The drawbacks of P&T are its complexity and the interference of water vapor generated in the purge [2]. According to this method were detected VOCs such as BTEX, chlorinated hydrocarbons, halomethanes and other volatiles in waters. A variety of sample preparation methods is available for extraction of contaminants in water. However, solid-phase extraction (SPE) is the method of choice that is particularly well adapted to multi-residue analysis, including a wide range of analytes of different polarities and physico-chemical properties, because of the great variety of sorbents available, their larger capacity as compared to microextraction techniques and moderate consumption of organic solvents and easy automation in contrast with liquid–liquid extraction [14]. HS analysis is a technique to separate and to collect VOCs in the gas phase from water samples. HS techniques have been very popular and widely used in the analysis of VOCs in various types of waters [15]. The next most popular methods of concentration needed analytes is solid-phase microextraction (SPME). The advantage of HS-SPME techniques is that the VOCs of the sample can be analyzed directly without any interference so as to reduce the possibility of matrix effects. This method is very reproducibility because of the entire analysis occurs in vacuum system. This method demonstrated good results for determination 53 chloroorganics in wastewaters, treated waters and river waters from Russia [16]. Studies of Swiss lake waters on contamination BTEX and methyl tert-butyl ether were carried out by HS-SPME technique with a Combi-PAL auto sampler to the pre-concentration of waters to obtain good reproducibility. These values were reported to be much better than HS alone. The method of HS followed by SPME had sample-recovery values of 105–110% with good sensitivity and reproducibility [6]. HS-SPME method is successfully applied for the analysis of chlorinated volatiles [17], trihalomethanes [18], BTEX [19-21] in various types of water.

In this paper VOCs determination was carried out by SPME-GC-MS technique. Identification of VOCs in water was carried out by calculation of Kovats retention indices. This method of identification is more informative and convenient form of provision reliable data. Retention indices can be taken from reference books, scientific articles, from the library of mass spectra NIST, or calculated using a mathematical model. Thus, knowing the Kovats indices of n-alkanes we may calculate the retention times of organic compounds. There is one requirement for this method is using a non-polar column based on polydimethylsiloxane.

In this paper we were determined retention times of n-alkanes in the column DB-5MS for carrying out the calculation of retention times of volatile organic pollutants using Kovats retention index.

2 Experiments

2.1 Reagents and materials

Standard solution of n-alkanes (C_8-C_{30}) used for calculation of retention times for organic pollutants with using Kovats indices. Standard solution of PAHs (acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene) and pesticides (DDT, DDE, DDD) used for prepare a model sample for assay the results are obtained by calculating retention times of organic pollutants.

2.2 GC-MS analysis

Analysis of VOC in water samples were carried out using HT280T autosampler (HTA, Italy) installed on 6890N/5975C (Agilent, USA) GC-MS system equipped with a split/splitless injector and a mass spectrometer selective detector was used. The separation was performed with a DB-5MS non-polar column (30m x 0,25mm x 0,25μm). Helium was used as a carrier gas with a constant flow of 1 mL/min. The temperature program was held at 40°C for 2 min and increased at 10°C/min to 300°C for 30 min, temperature of MSD's interface – 240°C. A full-scan acquisition mode (m/z 35–950) was used for detection, and the sample sizes for n-alkanes were 0.2 μL.

2.3 SPME procedure

The SPME was performed on fiber 50/30 μm DVB/CAR/PDMS during 60 minutes with 90°C extraction temperature. The evaporator temperature was 240°C. For the calculating retention times of VOCs we used Kovats retention indices for each compound which were taken from the library NIST'08. SPME procedure was used for extraction VOCs in surface water from Almaty city (Kazakhstan).

3 Results and Discussion

3.1 Calculation the retention times of VOCs used Kovats indices

The table 1 shows the results of determination of the n-alkanes' retention times and number of hydrocarbon atoms and its appropriate Kovats indices.

Table 1 – The retention time and number of hydrocarbon atoms of n-alkanes

n-Alkanes	Kovats indices	Retention time, min	n-Alkanes	Kovats indices	Retention time, min	n-Alkanes	Kovats indices	Retention time, min
C8	800	10.38	C20	2000	43.60	C26	2600	53.88
C15	1500	32.58	C21	2100	45.50	C27	2700	55.37
C16	1600	35.08	C22	2200	47.32	C28	2800	56.94
C17	1700	37.33	C23	2300	49.06	C29	2900	10.38
C18	1800	39.53	C24	2400	50.73	C30	3000	32.58
C19	1900	41.61	C25	2500	52.33			

Using the retention times and Kovats indices of n-alkanes was build dependence, which allowed to calculate the logarithmic formula. By using this formula we were calculate retention times of organic pollutants: $\boldsymbol{y = 37.38 \ln(x) - 240.3}$, where, y - the retention times of organic pollutants, x - retention indices of organic compounds. In the method of EPA 8270C there is a list of the most of dangerous and common semi-volatile pollutants (about 250 compounds). Kovats retention indices for each compounds taken from the library NIST'08. Thus, using Kovats retention indices were calculated retention times of volatile organic contaminants. For analysis of volatile organic pollutants in water samples was established SIM method with the base ion and Kovats retention indices of compounds. SIM method was divided into 22 series detectable group. Therefore, when creating a SIM method we should make additional 5 ions from the beginning and the end of each group. The optimal retention time for each ion (dwell time) was 10 msec. Analysis of the model of water sample contaminated with PAHs (acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene) and pesticides (DDD, DDT, DDE). The result of experiment were established that the retention times of organic compounds obtained by calculation are different by experimental for 15% (Table 2). The greatest differences were registered for the semi-volatile compounds.

3.2 Screening of volatile organic compounds in Almaty lake-settler using SPME-GC-MS

SPME analysis was performed using parameters which have been defined above in experimental part. The real water samples were taken from 'Sorbulak' lake-settler which located in Almaty city. It is a natural closed reservoir to store treated wastewater of the city. There is reset wastewater which traversed biological and mechanical cleaning. 'Sorbulak' is considered to be the biggest lake-settler in CIS (Figure 1). The Table 3 shows the results of VOCs analysis in water sampled from 'Sorbulak' lake-settler. The results of analysis showed that the both of water sample from sanitary zone contain volatile organic compounds, such acetophenone, o-toluidine, 2-methyl-naphthalene, phthalic anhydride, propylthiouracil and etc.

Table 2 – Results of analysis of the model of water sample contaminated with PAHs and pesticides

№	Compounds	Basic ion	Additional ions	CAS Registry Number	Retention index	Calculated retention time, min
1	Acenaphthylene	152	151,153	208-96-8	31.9	31.9
2	Acenaphthene	154	153,152	83-32-9	32.5	32.7
3	Fluorene	166	165,167	86-73-7	35.3	35.2
4	Phenanthrene	178	179,176	85-01-8	39.5	39.8
5	Anthracene	178	176,179	120-12-7	38.5	40.0
6	Fluoranthene	202	101,203	206-44-0	44.5	45.5
7	Pyrene	202	200,203	129-00-0	45.1	46.6
8	4,4'-DDE	246	248,176	72-55-9	45.9	47.1
9	4,4'-DDD	235	237,165	72-54-8	47.5	48.9
10	4,4'-DDT	235	237,165	50-29-3	49.4	50.3
11	Benz(a)anthracene	228	229,226	56-55-3	50.7	52.4
12	Chrysene	228	226,229	218-01-9	50.8	52.6

Satellite image of “Sorbulak” lake-settler

Image of “Sorbulak” lake-settler (July, 2013)

Figure 1 – “Sorbulak” lake-settler, Almaty (Kazakhstan)

Table 3 – Results of analysis of water samples from sanitary zone of “Sorbulak”

#	Compounds	Retention time, min	Basic ion	Peak area, $\times10^{-3}$	#	Compounds	Retention time, min	Basic ion	Peak area, $\times10^{-3}$
1	2,3-Diamino-2,3-Dimethylbutane	7.79	58	204.1	35	N-(Pentafluorosulfanyl) urea	21.45	44	6.8
2	3-Octanamine	8.06	58	6.1	36	1H-Imidazole, 1-methyl-5-nitro-	21.51	127	16.0
3	2-Propanol, 1-chloro-	8.29	45	6134.0	37	Phenol, 4-propoxy-	21.59	110	105.0
4	Ethyldiethanolamine	11.01	102	35.8	38	5-Methyl-4-nitro-1H-pyrazole	21.69	110	140.1
5	l-Proline, n-propargyloxycarbonyl-, propargyl ester	12.93	152	955.5	39	1,3-Benzodioxole, 2-methoxy-	22.00	121	27.0
6	2,5-Dimethyl pyrimidine	13.53	42	102.1	40	Pyridine, 2,6-dimethoxy-	22.12	139	32.6
7	Acetic acid, ethoxy-, ethyl ester	13.91	45	10.4	41	3-Cyclohexylcyclohexanol	22.29	82	19.7

#	Compounds	Retention time, min	Basic ion	Peak area, $\times 10^{-3}$	#	Compounds	Retention time, min	Basic ion	Peak area, $\times 10^{-3}$
8	Diazirine	14.08	14	38.5	42	N-(Dimethyl thiophosphinyl)-2-butylamine	22.38	72	746.6
9	Dimefox	14.63	44	47.1	43	2,3-Pyridine-dicarboxylic acid, dimethyl ester	22.55	79	49.0
10	3-Amino-4-pyrazolecarbonitrile	14.90	108	34.2	44	Cyclohexene, 1-methyl-4-(1-methylethyl)-, (R)- (p-Menthene)	22.73	95	23.1
11	4H-1,3-Benzodioxin	15.03	78	6.2	45	3-Acetyl-2,5-dimethyl thiophene	22.88	139	68.6
12	2,5-Pyrrolidinedione, 1-(benzoyloxy)-	15.20	105	89.7	46	Etamiphyllin	23.02	86	35.1
13	Methanesulfinyl fluoride	15.27	67	11.6	47	3,4-Diamino-1,2,4(4H)-triazole	23.11	99	807.8
14	Benzaldehyde, 2-nitro-, phenylhydrazone	15.48	77	31.1	48	tri-n-Amylphosphate	23.24	99	131.8
15	Benzoin	16.10	105	109.5	49	Phosphonous difluoride, 1,2-ethanediylbis-	23.30	69	44.5
16	2H-Pyran-2,6(3H)-dione, dihydro-	16.19	42	13.9	50	Fumaric acid, 3-fluorophenyl pentyl ester	23.37	169	41.9
17	3,7-Dimethyl-1,7-octadien-3-amine	16.45	70	5.9	51	1-Butanamine, N-nitro-	24.03	75	101.9
18	Phenacylidene diacetate	16.56	105	132.7	52	Dithiobiuret	25.13	119	142.1
19	6-exo-Vinyl-5-endo-norbornenol	16.97	70	108.8	53	Uracil, 6-acetamido-	25.23	127	180.8
20	5-Amino-3-azido-1,2,4-triazine-6-carbonitrile	17.34	54	43.6	54	4-Methyl-2-nitroimidazole	25.33	127	14.3
21	1H-1,2,4-Triazole, 1-(2-propenyl)	18.09	108	17.0	55	4-Methyl-1-nitropyrazole	25.39	127	10.6
22	Pyridine-3-carboxamide, N-(3-hydroxypropyl)	18.24	106	13.2	56	t-Butyl cyclopentaneperoxycarboxylate	25.428	41	76.1
23	(2H)Pyrrole-2-carbonitrile, 5-amino-3,4-dihydro	18.38	81	19.8	57	Urea, N,N-dimethyl-N'-phenyl	25.48	72	13.1
24	Pyridine, 3-methyl-, 1-oxide	18.46	109	15.9	58	Uracil, 6-acetamido-	25.71	127	68.9
#	Compounds	Retention time, min	Basic ion	Peak area, $\times 10^{-3}$	#	Compounds	Retention time, min	Basic ion	Peak area, $\times 10^{-3}$
25	dl-Noformicin sulfate	18.76	83	78.7	59	1H-Indole, 5-methyl-2,3diphenyl-	26.42	283	759.4
26	Carbonochloridic acid, 2-bromoethyl ester	19.02	106	16.4	60	2-Tetrazene, 1,1,4,4-tetrakis(1-methylethyl)	26.54	58	80.9
27	Formic acid, pyridin-2-ylmethyl ester	19.28	93	20.0	61	Urea, N-phenyl-N'-1H-purin-6-yl	27.08	93	370.3
28	Phenol, 4-amino-	19.59	109	6.8	62	Azinphos-methyl	27.55	160	42.3
29	2-Pyrazoline-1-carboxamide, 3-methyl	19.75	83	181.3	63	1,3,5-Trimethyl-2-(2,2,2-trifluoro-ethoxy)-benzene	27.61	135	173.3
30	2(1H)-Pyrimidinethione, 4,6-diamino-	19.96	142	9.6	64	5-Thiazoleacetic acid, 4-methyl	27.67	112	24.1
31	1,3-Dimethyl-2,4,5-trioxoimidazolidine	20.42	142	71.5	65	3-Methylthio-6-phenyl-5-thioxo-2,5-dihydro-triazine	27.85	134	4.7
32	2,3,4,5-Tetrahydropyridazine	20.82	84	38.6	66	Pyridine, 2-fluoro-5-iodo	28.05	223	4984.8
33	Benzenethiol	20.96	110	153.4	67	Pyrido[2,3-d] pyrimidine, 4-ethyl	28.18	158	6.6
34	2H-1,2,3-Triazol-4-amine, 2-methyl-5-nitro-	21.3	43	522.3	68	N-(4-Aminophenyl)-N'-phenyl-urea	28.88	108	25.3

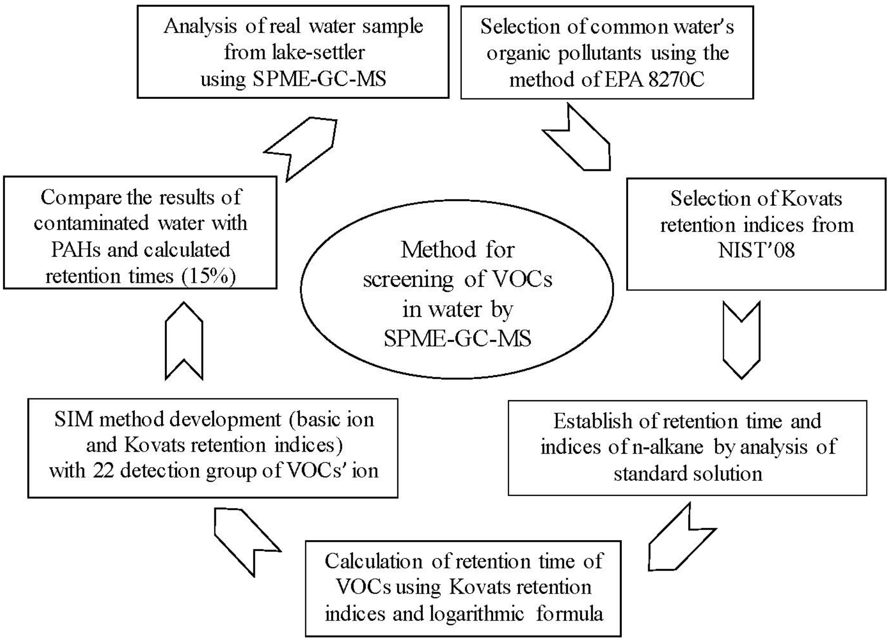

Figure 2 – Methodology of screening VOCs in water samples by SPME-GC-MS

Conclusion

This paper conducted a research and defined a set of database of retention time, basic ions, CAS number and Kovats retention indices of VOCs from EPA 8270C. The compounds were divided into 22 groups to develop sensitivity SIM method for SPME-GC-MS analysis. Methodology for VOCs determination in water samples was presented in Figure 2.

Using the retention times and retention indices of n-alkanes dependence was built, which allowed to calculate the retention times of 210 organic pollutants. Also this method was successfully applied for analysis of water from Almaty Lake-Settler. As a result 68 main organic compounds were identified, including phenolic compounds, pesticides and polyaromatic hydrocarbons.

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ҚФМЭ-ГХ-МС ӘДІСІМЕН АЛМАТЫ СУТҰНДЫРҒЫСЫ СУЫНДА ҰШҚЫШ ОРГАНИКАЛЫҚ ЛАСТАУШЫЛАРДЫҢ СКРИНИНГІ

Аннотация. Ірі қалалардың экологиялық мәселелері, яғни тұрмыстық және өндірістік қалдықтардың жинақталуы халықтың тығыз орналасуымен, жоғары мөлшерде өндірістік және тұрмыстық шығындардың себебі болатын өндірістердің дамуы және транспорттың көп болуымен тікелей байланысты. Бұл қалдықтар химиялық қосылыстардың суда еритін әрі оны ластайтын ұшқыш және ұшқыштығы нашар улы органикалық қосылыстар түрлерінен болуы мүмкін. Нәтижесінде, ластанған суды одан әрі тазартуға арналған арнайы сутұндырғы бар. Улы органикалық қосылыстардың ауыз суға түсу мүмкіншілігін және қоршаған ортаға залал келтіруін болдырмау үшін, осындай сутұндырғылардың жыл сайынғы мониторингін жүргізу қажет.

АҚШ-ң қоршаған ортаны қорғау жөніндегі агенттігі қоршаған ортадағы ұшқыш және орташа ұшқыш органикалық қосылыстарды газды хроматография масс-спектрометрия (ГХ/МС) әдісі бойынша анықтау үшін EPA 8270S әдісін ұсынды. Алайда бұл әдіс, калибровкалық қисықты тұрғызу үшін бағалы стандартты үлгілерді қолдануды, экстракция үшін барлық 210 қосылыстардың және органикалық еріткіштердің ұстау уақытын белгілеуді қажет ететіндіктен экономикалық тиімсіз болып табылады.

Бұл жұмыстың мақсаты бағалы стандарттық үлгілерді және экстракция үшін органикалық еріткіштерді қолданусыз судағы ұшқыш органикалық қосылыстарды анықтаудың жаңа селективті, ақпаратты және эффективті «жасыл» әдісін жетілдіру болып табылады. Ковач ұстау индексі бойынша шыңдарды анықтаудың ГХ/МС әдісімен үйлесім тапқан қатты фазалы микроэкстракция әдісі, қоршаған орта нысанындағы ұшқыш органикалық қосылыстарды анықтау үшін барлық талаптарға жауап беретін ең қолайлы әдіс болып табылады. Бұл «жасыл» әдіс қоршаған орта нысанындағы ұшқыш органикалық қосылыстарды анықтауға мүмкіндік береді. Жұмыстың нәтижелері қатты фазалы микроэкстракцияның параметрлерін оңтайландыруды және қалыпты алкандардың ұстау уақытын есептеуді қамтыды. Қалыпты алкандардың ұстау уақытын және ұстау индексін қолдана отырып, 210 органикалық ластағыштардың ұстау уақытын есептеуге мүмкіндік беретін тәуелділік графигі тұрғызылды. Сонымен қатар, бұл әдіс Алматылық «Сорбұлақ» сутұндырғысының суларын талдау үшін сәтті қолданылды және 68 негізгі органикалық қосылыстар, соның ішінде, фенолды қосылыстар, пестицидтер, полиароматты көмірсутектер анықталды.

Түйін сөздер: ұшқыш органикалық қосылыстар, Ковач индексі, қатты фазалы микроэкстракция, газды хроматография, масс-спектрометрия.

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СКРИНИНГ ЛЕТУЧИХ ОРГАНИЧЕСКИХ ЗАГРЯЗНИТЕЛЕЙ В ВОДЕ АЛМАТИНСКОГО ВОДООТСТОЙНИКА МЕТОДОМ ТФМЭ-ГХ-МС

Аннотация. Экологические проблемы крупных городов напрямую связаны с высокой концентрацией населения, развитой промышленностью и большим количеством транспорта, что является причиной большого количества промышленных и бытовых выбросов. Эти выбросы могут представлять собой различные виды химических соединений: летучие, полулетучие и токсичные органические соединения, которые могут растворятся в воде, тем самым загрязняя ее. В результате этого существуют так называемые водоотстойники, где загрязненная вода хранится для дальнейшей очистки. Для предотвращения возможности попадания вредных органических соединений в питьевую воду и нанесения ущерба окружающей среде, необходимо проводить ежегодный мониторинг таких водоотстойников. Агентство по охране окружающей среды США предложило метод EPA 8270S для определения летучих и полулетучих органических соединений в объектах окружающей среды методом газовой хроматографии с масс-спектрометрическим детектированием (ГХ/МС). Однако, этот метод является экономически невыгодным, так как он требует применения дорогостоящих стандартных образцов для построения калибровочной кривой, и установленное время удерживания всех 210 соединений и органических растворителей для экстракции.

Целью данной работы является разработка нового селективного, информативного и эффективного «зеленого» метода обнаружения летучих органических соединений в воде без использования органических растворителей для экстракции и дорогостоящих стандартных образцов. Метод твердофазной микроэкстракции в сочетании с ГХ/МС с определением пиков по индексу удерживания Ковача является наиболее подходящим методом, отвечающий всем требованиям для обнаружения летучих органических соединений в объектах окружающей среды. Этот «зеленый» метод позволит определить летучие органические соединений в объектах окружающей среды. Результаты работы включали в себя оптимизацию параметров твердофазной микроэкстракции и расчета времени удерживания н-алканов. Используя времена удерживания и индексов удерживания н-алканов, была построена зависимость, что позволило рассчитать время удерживания 210 органических загрязнителей. Кроме того, этот метод был успешно применен для анализа воды из Алматинского водоотстойника «Сорбулак» и были идентифицированы 68 основных органических соединений, в числе которых фенольные соединения, пестициды и полиароматические углеводороды.

Ключевые слова: летучие органические соединения, индекс Ковача, твердофазная микроэкстракция, газовая хроматография, масс-спектрометрия.