

Gas chromatography–mass spectrometry with headspace for the analysis of volatile organic compounds in waste water

V.I. Safarova^a, S.V. Sapelnikova^{b,*}, E.V. Djazhenko^b, G.I. Teplova^a,
G.F. Shajdulina^a, F.Kh. Kudasheva^{b,1}

^a Department of the State Analytical Monitoring, Ufa, Russia

^b Analytical Chemistry Department, Bashkir State University, Ufa, Russia

Abstract

Headspace analysis combined with high-resolution gas chromatography and detection by mass spectrometry was evaluated for the analysis of 53 volatile organic compounds (VOCs) in river waters, waste waters and treated water samples down to $0.1 \mu\text{g l}^{-1}$ concentration levels. The conditions optimised included sample thermostating time and temperature, autosampler parameters and the nature of salt, added to the sample. The pollutions origin and their seasonal rippling have been done. It was shown that the content of VOCs in river water mainly correlates to the content of these compounds in waste waters, which shows the anthropogenic character of the pollutions.

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1. Introduction

The anthropogenic pollution of environmental water goes into the global scales, thus representing significant public health risk. Volatile organic compounds (VOCs) have been shown to affect a wide number of biological and environmental systems, they influence various atmospheric processes, some are carcinogens and/or mutagens, while others are persistent and show bioaccumulation effects [1]. In addition, many VOCs exhibit toxic effects on aquatic organisms.

As regards the water, VOCs are among the most commonly found contaminants in groundwater. Their volatility is the reason they are not often found in concentrations above a few $\mu\text{g l}^{-1}$ in surface waters, but in groundwater their concentrations can be hundreds or thousands of times higher [2]. Trace levels of monocyclic aromatic hydrocarbons and halocarbons have even been found in Antarctic waters and surface snows [3]. VOCs, including halogens and halocarbons that are produced by marine algae and phytoplankton, may cause ozone depletion in the troposphere and stratosphere [4].

VOCs occur in numerous products including fuels, solvents, paints, adhesives, deodorants, and refrigerants. VOCs also occur in combustion exhausts and especially trihalomethanes occur in chlorinated drinking water. VOCs are released into the environment during their production, distribution, storage, handling, and use and can enter both surface water and ground water supplies from many point and non-point sources. Identifying the sources of VOCs in urban waters and determining which sources have the greatest effect on water quality are critical steps in protecting source-water quality and prioritising contaminant-control measures [5].

For the determination of VOCs in water, direct aqueous injection of sample [2], static headspace (HS) techniques [6], dynamic headspace techniques [4,7,8], liquid–liquid extraction [2], membrane techniques [9,10], solid-phase extraction, solid-phase microextraction [11–15] and distillation techniques are used as sample preparation techniques. Because of low concentration levels found in natural waters (ng l^{-1} to $\mu\text{g l}^{-1}$) a preconcentration step is necessary prior to analysis and detection.

Despite the fact that the detection limits of the static headspace technique are more than 10 times higher than those of the dynamic (purge and trap) technique [16], there are two drawbacks of the last one: first, it requires complex instrumentation, and second disadvantage is related to the

* Corresponding author. Tel.: +7-3472-236721; fax: +7-3472-236680.

E-mail addresses: sapelnikovasv@ic.bashedu.ru (S.V. Sapelnikova), kudashevafh@bsu.bashedu.ru (F.Kh. Kudasheva).

¹ Co-corresponding author.

water vapour generated at the purge stage [17]. The best qualities of the headspace gas chromatography (HS-GC) method are the wide dynamic range and simpler instrumentation then for purge and trap technique [16], combining with rather low detection limits (from $0.03 \mu\text{g l}^{-1}$ [6]). HS involves the partitioning between the VOCs concentration in a water sample and the concentration in the gaseous phase above the water. According to this method a quantity of HS over a sample is removed and injected directly into a GC, therefore only liquid–gas equilibrium is involved [2].

The objectives of this work were two-fold. First the applicability of HS combined with gas chromatography–mass spectrometry (GC–MS) was investigated towards the analysis of 53 VOCs, e.g., chlorinated alkanes and alkenes, mono- and polycyclic aromatic hydrocarbons and chlorinated monocyclic aromatic hydrocarbons, in waste waters of 10 industries, treated water and 10 rivers water taken from different sampling points in Ufa (Russia) region. Second, besides the development of analytical method, the analysis of the pollution origin and their seasonal rippling has been done.

2. Experimental

2.1. Apparatus

The GC system used was a Hewlett-Packard (San Jose, CA) Model 5890 Series gas chromatograph equipped with a Model 5989B mass-selective detector, which allows scanning in a range from 1 up to 1000 units of mass and is equipped with hyperbolic quadruple of mass analyser and secondary multiplier with the high-voltage conversion diode for the reduction of mass discrimination.

The HP 7694 headspace autosampler was used to introduce samples automatically directly into a GC. A low-volume, highly inert, heated volatiles interface is optimised for HS-GC analysis, preventing sample loss or degradation and reducing carryover. HP Vectra 486/66 MX computer with HP 5895A Chemstation software was used for the evaluation of data.

Chromatographic separation was achieved on a J&W Scientific DB-1701 capillary column, $30 \text{ m} \times 0.32 \text{ mm}$ i.d., containing 14% cyanopropylphenylmethylpolysiloxane.

2.2. Reagents

The mixture of 53 VOCs calibration stock solution was purchased from HP, catalog no. 8500-6027, containing compounds at $200 \mu\text{g ml}^{-1}$ in methanol. The mixture of chlorobenzene- d_5 , 1,4-difluorobenzene, 1,4-dichlorobenzene- d_4 and pentafluorobenzene at concentrations of each $200 \mu\text{g ml}^{-1}$ (HP catalog no. 8500-5902), d_8 -toluene, d_6 -benzene, d-chloroform (TC 95 596-86E, Isotope, St. Petersburg, Russia) were used as internal standard. Chloro-

Table 1
Analytical conditions of headspace GC–MS system

Injector temperature	220 °C
Flow rate	5 ml min ⁻¹ during 0.2 min, then 1.5 ml min ⁻¹
Carrier gas	He
Factor of division	1:6
Oven temperature	32 °C during 5 min, then from 32 up to 220 °C with gradient 6 °C min ⁻¹
Ion source temperature	200 °C
Ion source vacuum	2×10^{-5} mmHg
Ion ionised energy	70 eV
Electrons' emission current	30 mA

form, dichloroethane, perchloroethylene, trichloroethylene and toluene were purchased from Supelco, Bellefonte, PA.

Calibration aqueous solutions were prepared by suitable dilution of calibration stock standards solution in water obtained from Millipore Milli-Q purification system (Bedford, MA).

2.3. Sampling

Sampling was performed seasonally, from October 1999 to September 2000, three times during each season, at 10 industrial sewages, 11 rivers and 1 water treatment plant. The sampling points on the rivers have been established in different distances, up- and down-stream, from industrial waste waters. Samples for VOCs measurements were collected from each sampling point in 40–120 ml glass vials. Each vial was filled to capacity to avoid any headspace. All the samples were kept at 4 °C and analysed immediately after sampling.

2.4. Procedure

For calibrating curves standard solutions of VOCs were made in the vials treated with nitrogen beforehand. The prepared samples after ultrasonic treatment during 5 min were put into the headspace autosampler. Headspace GC–MS analysis and detection were carried out under conditions listed in Table 1.

3. Results and discussion

In order to increase the extraction of volatile organic compounds from aqueous solution, parameters of headspace analysis were optimised. The influence of sample thermostating temperature, autosampler parameters, nature of added salt have been studied on the model mixtures. Standard solutions of VOCs ($20 \mu\text{g ml}^{-1}$) with the internal standards were chosen as the model mixtures. The efficiency of headspace extraction was checked by

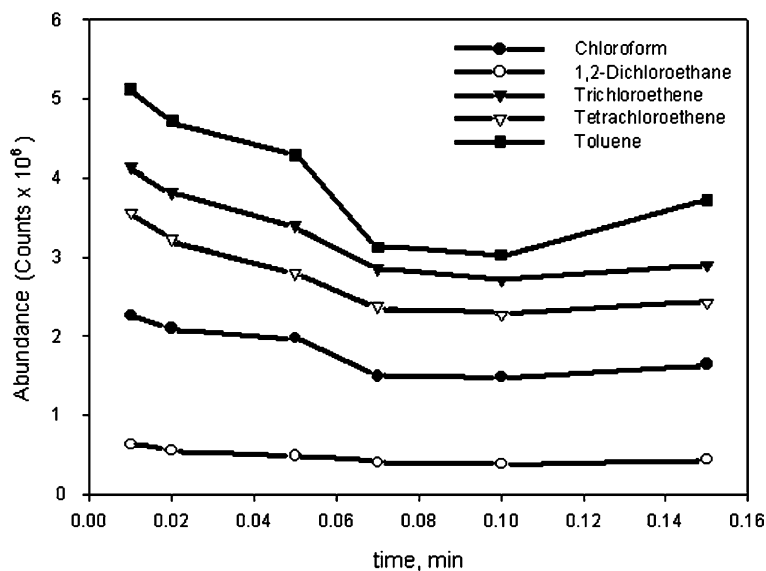


Fig. 1. The influence of time of balance establishment in the loop of autosampler on the VOCs abundance.

comparison with chloroform, dichloroethane, perchloroethylene, trichloroethylene and toluene. The choice of given compounds was determined by the fact, that the method was supposed to be used in the region of industrial sector, where the main pollutants found before were chlorinated aliphatic compounds and mentioned above substances among them.

The nature of the salt was found to have a great influence to the VOCs extraction. The highest extraction can be achieved by using monocharged cation and anion, respectively. For further experiments KCl was chosen. The influence of the time of balance establishment in the loop of autosampler is shown in Fig. 1. The shortest period is the most optimum for the procedure. Injection time was found to have the less influence on the peak areas, it was chosen to use 0.5 min injection nevertheless this parameter can be varied without decreasing in sensitivity. The optimised time of loop filling is 0.1 min (data not shown).

Chromatographic characteristics of analysed compounds, including retention time and characteristic ion, are presented in Table 2. Calibrations have been made in the interval from 0.5 to 100 $\mu\text{g l}^{-1}$ with mean correlation coefficients of 0.995.

Chromatogram of one blank water sample with a standard mixture of VOCs is shown in Fig. 2 as an example.

The sampling points were planned in order to look after contents and concentrations of the substances simultaneously from the places of their possible dump after technological process through biological treatment plants up to the natural reservoirs within 200 km from the industrial sewage.

Average year concentrations of VOCs in industrial sewage and Belaya River are presented in Table 3. No attempts were made to decrease the detection limits, because obtained sensitivity was significantly lower than the maximum allowable concentrations for the studied water types.

There is evident correlation between the distance from the industrial zone and the content of organic compounds in water. In the river the decrease of pollutant content was achieved due to the processes of purification of the reservoir: dilution, bio-degradation of acting substances of waste water and transformation of polluting compounds.

In order to find out the sources of Belaya River pollution, 10 inflow rivers samples were analysed. In these samples, chlorinated impurities were not found at all, and the average

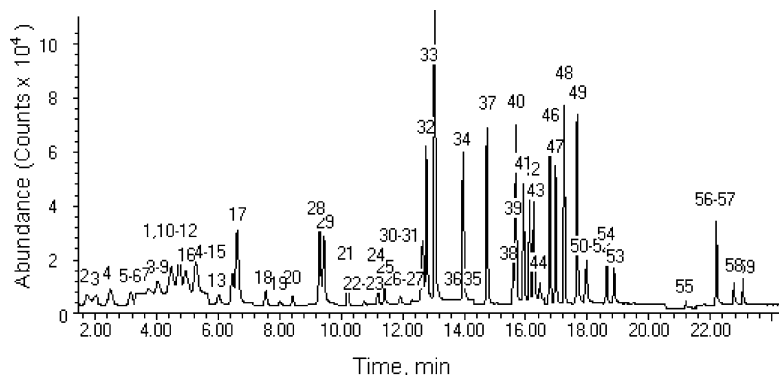


Fig. 2. Chromatogram of a standard solution of VOCs (see Table 2) obtained by headspace GC–MS analysis.

Table 2
Chromatographic characteristics of the target compounds

No.	Substance	Retention time (s)	Characteristic ion (<i>m/z</i>)
1	d ₁ -Chloroform (internal standard)	5.05 ± 0.05	86
2	1,1-Dichloroethene	1.75 ± 0.02	61
3	Dichloromethane	2.49 ± 0.02	84
4	<i>trans</i> -1,2-Dichloroethene	2.57 ± 0.03	61
5	1,1-Dichloroethane	3.28 ± 0.03	63
6	2,2-Dichloropropane	3.94 ± 0.04	77
7	<i>cis</i> -1,2-Dichloroethene	4.23 ± 0.04	61
8	1,1,1-Trichloroethane	4.68 ± 0.04	97
9	Carbon tetrachloride	4.72 ± 0.05	119
10	Bromochloromethane	4.81 ± 0.05	130
11	1,1-Dichloropropene	4.96 ± 0.05	110
12	Chloroform	4.99 ± 0.05	83
13	1,2-Dichloroethane	6.29 ± 0.06	62
14	d-Benzene (internal standard)	5.56 ± 0.06	84
15	Benzene	5.61 ± 0.06	77
16	Pentafluorobenzene (internal standard)	5.24 ± 0.05	168
17	Trichloroethene	6.89 ± 0.07	132
18	1,2-Dichloropropane	7.85 ± 0.08	63
19	Dibromomethane	8.29 ± 0.08	174
20	Bromodichloromethane	8.72 ± 0.09	83
21	Tetrachloroethene	10.51 ± 0.11	166
22	<i>cis</i> -1,3-Dichloropropene	9.56 ± 0.10	75
23	<i>trans</i> -1,3-Dichloropropene	11.05 ± 0.	75
24	1,1,2-Trichloroethane	11.49 ± 0.11	97
25	1,3-Dichloropropane	11.71 ± 0.12	76
26	Dibromochloromethane	12.20 ± 0.12	129
27	1,2-Dibrommethane	12.22 ± 0.12	107
28	d ₈ -Toluene (internal standard)	9.64 ± 0.10	98
29	Toluene	9.74 ± 0.10	91
30	d ₅ -Chlorobenzene (internal standard)	12.95 ± 0.13	117
31	Chlorobenzene	12.98 ± 0.13	112
32	Ethylbenzene	13.07 ± 0.13	91
33	<i>m-p</i> -Xylene	13.35 ± 0.13	91
34	<i>o</i> -Xylene	13.07 ± 0.13	91
35	Styrene	14.29 ± 0.14	104
36	1,1,1,2-Tetrachloroethane	13.38 ± 0.13	131
37	Isopropylbenzene	15.06 ± 0.15	105
38	Bromoform	15.37 ± 0.15	173
39	Bromobenzene	15.93 ± 0.15	156
40	Propylbenzene	15.99 ± 0.16	91
41	2-Chlorotoluene	16.26 ± 0.16	91
42	1,3,5-Trimethylbenzene	16.44 ± 0.16	105
43	4-Chlorotoluene	16.59 ± 0.17	91
44	1,2,3-Trichloropropane	16.77 ± 0.17	75
45	1,1,2,2-Tetrachloroethane	16.88 ± 0.17	83
46	<i>tert</i> -Butylbenzene	17.13 ± 0.09	119
47	1,2,4-Trimethylbenzene	17.30 ± 0.09	105
48	<i>sec</i> -Butylbenzene	17.59 ± 0.09	105
49	4-Isopropyltoluene	17.99 ± 0.09	119
50	d ₄ -1,4-Dichlorobenzene (internal standard)	18.28 ± 0.09	152
51	1,3-Dichlorobenzene	18.01 ± 0.09	146
52	1,4-Dichlorobenzene	18.30 ± 0.09	146
53	1,2-Dichlorobenzene	19.19 ± 0.10	146
54	Butylbenzene	18.97 ± 0.09	134
55	1,2-Dibrom-3-chloropropane	21.48 ± 0.11	157
56	1,2,4-Trichlorobenzene	22.45 ± 0.11	180
57	1,2,3-Trichlorobenzene	23.30 ± 0.12	180
58	Naphthalene	22.98 ± 0.11	128
59	Hexachlorobutadiene	22.45 ± 0.11	225

Table 3
Content of prior pollutants in waste water and Belaya River

Substance	Year average concentration (mg l ⁻¹)				Maximum allowable concentration (mg l ⁻¹) [18]	
	Belaya River	Waste water	Belaya River		Fishery water	Municipal water
	Above industrial zone		Below industrial zone	200 km from industrial zone		
1,1-Dichloroethene	<0.0001	0.0123 ± 0.0006	<0.0001	<0.0001	0.1	0.0006
<i>cis</i> -1,2-Dichloroethene	<0.0001	0.0036 ± 0.001	<0.0001	<0.0001	–	–
Carbon tetrachloride	<0.0001	0.0108 ± 0.001	0.0005 ± 0.0005	<0.0001	0.001	0.006
2,3-Dichloropropene	<0.0001	0.0659 ± 0.004	<0.0001	<0.0001	–	–
Chloroform	<0.0001	0.0513 ± 0.003	0.0018 ± 0.0006	<0.0001	0.005	0.06
1,2-Dichloroethane	<0.0001	0.2917 ± 0.008	0.0051 ± 0.0009	0.0006	0.1	0.02
Trichloroethene	<0.0001	0.0106 ± 0.001	0.0008 ± 0.0006	<0.0001	0.01	0.06
1,2-Dichloropropane	<0.0001	0.4103 ± 0.0008	0.0055 ± 0.001	<0.0001	–	0.4
Bromodichloromethane	<0.0001	0.0088 ± 0.001	<0.0001	<0.0001	–	0.03
Tetrachloroethene	<0.0001	0.0097 ± 0.0009	0.0006 ± 0.0004	<0.0001	0.16	0.02
<i>cis</i> -1,3-Dichloropropene	<0.0001	0.0076 ± 0.0009	0.0002	<0.0001	–	0.4
<i>trans</i> -1,3-Dichloropropene	<0.0001	0.0106 ± 0.001	0.0001	<0.0001	–	1.4
1,1,2-Trichloroethane	<0.0001	0.0123 ± 0.001	0.0004 ± 0.0004	<0.0001	–	–
1,3-Dichloropropane	<0.0001	0.0004 ± 0.0004	<0.0001	<0.0001	–	–
Dibromochloromethane	<0.0001	0.0048 ± 0.0009	<0.0001	<0.0001	–	0.03
1,1,1,2-Tetrachloroethane	<0.0001	0.0018 ± 0.0006	<0.0001	<0.0001	–	0.2
Bromoform	<0.0001	0.0021 ± 0.0007	<0.0004	<0.0001	0.001	–
1,2,3-Trichloropropane	<0.0001	0.1422 ± 0.004	0.0016 ± 0.0005	<0.0001	–	0.07
1,1,2,2-Tetrachloroethane	<0.0001	0.0040 ± 0.001	<0.0001	<0.0001	–	0.2
1,2,2,3-Tetrachloropropane	<0.0001	0.0027	<0.0001	<0.0001	–	–
Benzene	<0.0001	0.0029 ± 0.0005	0.0001	<0.0001	0.5	0.5
Toluene	<0.0001	0.0057 ± 0.0006	0.0009 ± 0.0005	<0.0001	0.5	0.5
<i>m</i> -/ <i>p</i> -Xylene	<0.0001	0.0013 ± 0.0004	0.0001	<0.0001	–	0.05
<i>o</i> -Xylene	<0.0001	0.0028 ± 0.0006	0.0001	<0.0001	0.05	0.05
1,3,5-Trimethylbenzene	<0.0001	0.0003 ± 0.0004	0.0001	<0.0001	0.5	–
1,2,4-Trimethylbenzene	<0.0001	0.0008 ± 0.0004	0.0001	<0.0001	0.5	–
Naphthalene	<0.0001	0.0012 ± 0.0005	0.0012 ± 0.0005	<0.0001	0.04	0.01

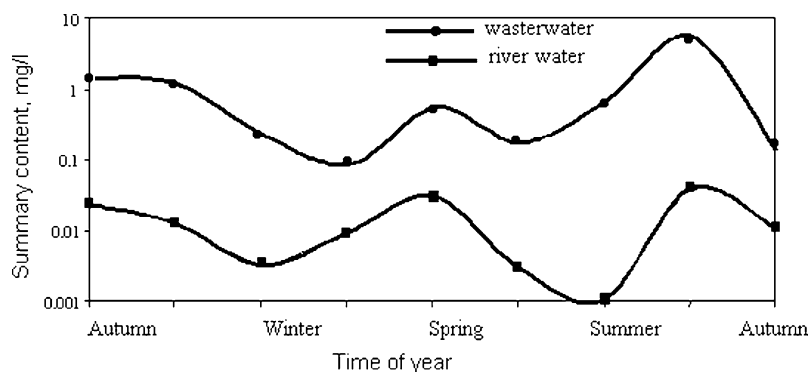


Fig. 3. Summary content of chloroorganic compound in: (●) waste water from industrial zone; (■) Belaya River below industrial zone.

year concentrations of benzene and toluene did not exceeded value of 0.0001 mg l⁻¹.

Seasonal profiles of VOCs are complex and highly dependent on the local environment and meteorological conditions. The summary content of volatile chlorinated compounds in waste water and river water during the whole year is presented in Fig. 3. The definite resembling of the two curves (one for waste water and other for river water) allows making a conclusion about anthropogenic origin of the pollution.

4. Conclusions

Static headspace GC–MS was optimised for the detection of 53 volatile organic compounds in river waters, industrial waste waters and treated water. The evaluation of pollution source together with seasonal rippling has been done. The study of summary contents of chloroorganic compounds in waste and surface waters inside the distance up to 200 km from the industrial sewage zone clearly shows the anthropogenic nature of the river pollutions.

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