

Rapid liquid–liquid extraction for the reliable GC/MS analysis of volatile priority pollutants

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Abstract Mass spectrometry is a powerful tool for the analysis of organic pollutants in the environment. Nevertheless, sample preparation for GC/MS analysis is often criticized for being too laborious and requiring expensive equipment. Thus, purge-and-trap or headspace devices are the most popular nowadays to investigate volatile organic pollutants. At the same time, modern commercial high-resolution mass spectrometers allow for the significant simplification of the sample preparation procedures due to better acquisition rate, accurate mass measurements, and improved sensitivity. Here, we used a time-of-flight high-resolution mass spectrometer Pegasus GC-HRT (LECO, USA) to identify and quantify 47 volatile priority organic pollutants in water. The developed accelerated water sample preparation approach requires just 1 mL of water and 1 mL of dichloromethane. The detection limits of the analytes are about $1 \mu\text{g L}^{-1}$, while the quantification limits are approximately $5 \mu\text{g L}^{-1}$. These limits correspond to those required by Method 8260C of the United States Environmental Protection Agency. Here, we demonstrate that sample preparation for the reliable and sensitive GC/MS analysis of volatile organic priority pollutants may be achieved in 5 min in 5-mL vials in the field or just prior to GC/MS analysis in the laboratory without the use of any expensive equipment.

Keywords Priority pollutants · Volatile compounds · Gas chromatography/mass spectrometry · High-resolution mass spectrometry · Quantitative analysis · Express analysis · Water sample preparation

Introduction

Mass spectrometry is the most reliable analytical tool to identify and quantify organic compounds in environmental samples (Lebedev 2013), while gas chromatography/mass spectrometry (GC/MS) has remained the method of choice for the targeted and non-targeted analysis of volatile and semivolatile pollutants. The benefits of GC/MS include the universality, speed, sensitivity, reliability, and the availability of mass spectral libraries (NIST 2014). Perhaps the only matter of concern when dealing with GC/MS involves sample preparation. In the majority of standard methods, the sample preparation procedure is laborious, time-consuming and often results in the losses of certain analytes or distorted results even in the case of rather simple matrixes like water (Method 8260C 2006; Method 8270D 2007). In the case of biota samples, the difficulties with sample preparation can be even worse (Sachs and Kintz 1998; Lebedev et al. 1998; Richardson et al. 1998; Vetter and Maruya 2000; Bayen et al. 2006; Santos et al. 2006; Baron et al. 2012; Andreu and Pico 2012; Agilent Technologies, Inc. 2013; Zhang et al. 2015). These issues have inspired significant efforts to develop faster, easier, and more reliable methods of sample preparation. Several recent reviews deal with these modern approaches (Ballesteros-Gomez and Rubio 2011; Zuloaga et al. 2012), while all the issues regarding miniaturized sample preparation are summarized in a recent book (Pena Pereira 2014).

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The most straightforward approach of mass spectrometric analysis involves ambient ionization methods (Huang et al. 2011; Harris et al. 2011; Lebedev 2015). However, in the case of complex environmental samples, it is desirable to have a separation step in order to detect and quantify individual analytes, including possible isomers.

Earlier, we reported on an AWASP method (Polyakova et al. 2012, 2014) for the fast, cheap, and reliable sample preparation of semivolatile compounds for GC/MS analysis requiring only 5 min. One of the advantages of this approach is the absence of any concentration step. As a consequence, there are no losses of analytes, while the recoveries for the semivolatile pollutants with higher vapor pressure (isomeric dichlorobenzenes, hexachloroethane, phenol and its methylated homologues, naphthalene) are significantly better than in the standard US EPA 8270 Method. The difference in recoveries is really dramatic in the case of aniline with 100 % recovery by AWASP and only 17 % recovery by EPA Method 8270 (Polyakova et al. 2014). AWASP was already successfully applied for the non-targeted analysis of the product of Miller–Urey experiment (Xie et al. 2015).

Therefore, we decided to apply the same AWASP approach for the analysis of volatile compounds which usually requires purge-and-trap (Method 8260C 2006) or headspace (Kolb and Ettre 1991, 2006) sample introduction followed by GC/MS analysis. These two popular approaches are constantly upgrading to satisfy the modern challenges (Pena Pereira 2014). Another approach for the analysis of volatile compounds involves solid-phase extraction using various polymeric sorbents (Pichon 2000; Żwir-Ferenc and Bizuk 2006) as well as its various forms including solid-phase microextraction (SPME) (Pawliszyn 1997) and stir bar sorptive extraction (SBSE) (Baltussen et al. 1999) followed by thermal desorption into the injector of a gas chromatograph.

Each of the above-mentioned methods has limitations in its analytical range when doing a complete screening analysis for organic components of various types. In this sense, classic liquid–liquid extraction still remains the most universal tool for the preparation of water samples, allowing for the extraction of various types of chemicals, especially when it deals with potential environmental pollutants. The concentration step is the main drawback of the classic liquid–liquid extraction, as a 100-fold solvent evaporation step unavoidably results in the loss of more volatile components. Thus, application of AWASP with the elimination of the concentration step (Polyakova et al. 2012, 2014) could overcome this shortcoming of the classic liquid–liquid extraction. In the present paper, we demonstrate the successful application of AWASP for the GC/MS analysis of volatile organic priority pollutants.

Materials and methods

Mass spectrometry and gas chromatography

All experiments were performed with a Pegasus[®] GC-HRT high-resolution time-of-flight (TOF) mass spectrometer (LECO Corporation, Saint Joseph, MI, USA) with a Folded Flight Path[®] multiple reflecting geometry mass analyzer coupled with an Agilent 7890A gas chromatograph (Agilent, Palo Alto, CA, USA). The instrument is capable of acquiring high-resolution (up to 50,000 at FWHH in ultra-high-resolution mode) and high-mass-accuracy (~ 1 ppm) data at a very high acquisition rate (up to 200 full mass range spectra per second). The system was controlled by ChromaTOF-HRT[®] software version 1.80 (LECO Corporation), which was also used for data collection and data processing. The data were collected using 10 full (10–500 m/z range) spectra per second in high-resolution mode (25,000 at FWHH). The electron ionization source was kept at 250 °C. Chromatographic separation was performed using an Rxi[®]-5Sil MS column of length 30 m, internal diameter 0.25 mm, and phase thickness 0.25 μm ; carrier gas–helium at constant flow of 1 mL min⁻¹; and the column temperature was programmed as follows: 33 °C (5 min), 10 °C/min to 160 °C; transfer line temperature—320 °C. Two microliters of sample was introduced into the injector heated at 250 °C at a split ratio of 10:1.

The chromatographic peaks were automatically found and quantified using the Target Analyte Finding feature of the ChromaTOF-HRT software, which uses mass accuracy of the molecular ions and certain characteristic fragment ions as part of the criteria for finding and matching analytes.

Chemical standards

Calibration solutions of volatile priority pollutants for all the experiments and solutions of internal standards (dibromofluoromethane, perdeuterotoluene, 1-bromo-2-fluorobenzene) were prepared from standard Restek (USA) mixtures. Distilled water used in the experiments was of HPLC grade. Dichloromethane (HPLC grade, $\geq 99.9\%$) and anhydrous granular sodium sulfate ($\geq 99.0\%$) were produced by Sigma-Aldrich (USA).

Sample preparation

One milliliter of the water sample was placed in a 5-mL vial, and 1 mL of dichloromethane was added. The sample was vigorously shaken for 1 min. Measured amounts of internal standards (10–20 ng) were added with a syringe to the organic phase, and then, ~ 1.8 g sodium sulfate was

Table 1 Analytes' response factors (RF) averaged for triplicate injections at four concentrations

Peak no.	Name	RF for various concentrations ng/mL				Average RF	SD	RSD %
		5	10	25	100			
1	<i>cis</i> -1,2-Dichloroethylene	1.3	1.2	1.2	1.1	1.2	0.06	5.0
2	2,2-Dichloropropane	0.62	0.76	0.82	0.74	0.74	0.08	11.4
3	Bromochloromethane	0.80	0.72	0.72	0.70	0.74	0.04	6.0
4	Chloroform ^a	7.7	4.6	2.7	1.6	1.5	2.65	64
5	1,1,1-Trichloroethane	0.70	0.84	0.82	0.82	0.80	0.06	8.1
6	1,2-Dichloroethane	0.46	0.52	0.56	0.62	0.54	0.07	13.0
7	1,1-Dichloropropene	1.3	1.2	1.2	1.0	1.2	0.12	10.1
8	Benzene	3.8	3.8	3.7	3.2	3.6	0.27	7.3
9	Carbon tetrachloride	0.84	0.86	0.84	0.76	0.83	0.04	5.4
10	Trichloroethylene	0.98	0.94	0.98	0.84	0.94	0.07	7.1
11	1,2-Dichloropropane	1.3	1.4	1.2	1.0	1.2	0.17	14.4
12	Dibromomethane	0.58	0.60	0.78	0.74	0.68	0.10	14.8
13	Bromodichloromethane	0.34	0.36	0.34	0.32	0.34	0.02	4.8
14	Toluene	1.5	1.4	1.3	1.2	1.3	0.13	9.4
15	1,1,2-Trichloroethane	0.20	0.26	0.28	0.28	0.26	0.04	14.8
16	1,3-Dichloropropane	0.38	0.40	0.44	0.44	0.42	0.03	7.2
17	Dibromochloromethane	0.24	0.30	0.32	0.32	0.30	0.04	12.8
18	Tetrachloroethylene	0.32	0.32	0.32	0.32	0.32	0.00	0.0
19	1,2-Dibromoethane	0.34	0.34	0.36	0.38	0.36	0.02	5.4
20	Chlorobenzene	0.66	0.76	0.72	0.72	0.72	0.04	5.8
21	1,1,1,2-Tetrachloroethane	0.20	0.22	0.22	0.24	0.22	0.02	7.4
22	Ethylbenzene	1.2	1.4	1.2	1.2	1.3	0.07	5.3
23	<i>m</i> + <i>p</i> Xylene	2.2	2.1	2.0	2.0	2.1	0.10	4.6
24	Bromoform	0.48	0.52	0.60	0.52	0.53	0.05	9.5
25	Styrene	1.3	1.4	1.5	1.3	1.4	0.07	5.2
26	<i>o</i> -Xylene	2.5	2.6	2.3	2.2	2.4	0.20	8.2
27	1,1,2,2-Tetrachloroethane ^a	2.1	1.6	1.5	1.2	1.4	0.36	23
28	Isopropylbenzene	2.7	2.7	2.5	2.2	2.5	0.22	8.9
29	1,2,3-Trichloropropane ^a	1.4	1.3	1.1	1.0	1.1	0.20	17
30	Bromobenzene	1.2	1.4	1.5	1.2	1.3	0.13	10.0
31	1-Chloro-2-methylbenzene	2.0	2.2	2.1	1.8	2.1	0.16	7.9
32	Propylbenzene	3.5	3.7	3.3	3.0	3.4	0.30	8.9
33	1-Chloro-4-methylbenzene	2.3	2.2	2.1	1.9	2.1	0.15	7.2
34	1,2,4-Trimethylbenzene	2.3	2.4	2.2	2.0	2.2	0.16	7.1
35	<i>tert</i> -Butylbenzene	1.7	1.8	1.8	1.5	1.7	0.13	7.8
36	1,2,3-Trimethylbenzene	2.5	2.3	2.2	2.0	2.2	0.19	8.6
37	1,3-Dichlorobenzene	0.94	1.2	1.2	1.2	1.2	0.14	12.3
38	<i>p</i> -Propyltoluene	2.7	2.8	2.8	2.5	2.7	0.15	5.7
39	1,4-Dichlorobenzene	1.0	1.3	1.4	1.2	1.2	0.16	13.4
40	<i>o</i> -Isopropyltoluene	2.1	2.0	2.0	1.8	2.0	0.14	7.3
41	1,2-Dichlorobenzene	1.0	1.2	1.2	1.2	1.1	0.10	9.2
42	Butylbenzene	2.3	2.5	2.4	2.2	2.3	0.12	5.2
43	1,2-Dibromo-3-chloropropane	0.24	0.32	0.38	0.38	0.33	0.07	20
44	1,2,4-Trichlorobenzene	0.66	0.80	0.90	0.84	0.80	0.10	12.7
45	Naphthalene	2.8	2.8	2.8	2.5	2.7	0.16	5.7
46	1,2,4-Trichlorobenzene	0.70	0.82	0.82	0.80	0.79	0.06	7.3

Table 1 continued

Peak no.	Name	RF for various concentrations ng/mL				Average RF	SD	RSD %
		5	10	25	100			
47	Hexachloro-1,3-butadiene	0.52	0.64	0.52	0.48	0.54	0.07	12.8

^a Average RF for these pollutants were recalculated taking into account their levels in the dichloromethane used as a solvent (see the text below)

introduced by small portions. The sample was vigorously shaken after each addition. After binding of the aqueous phase with sodium sulfate, the transparent dichloromethane extract was transferred into a clean vial for further analysis. Then, 2 μL of the extract was injected into the chromatograph at a split ratio of 10:1.

Results and discussion

Taking into account the sensitivity of modern GC/MS systems, it is definitely possible to significantly decrease the volume of an aqueous sample without degrading detection limits of the analysis. Since the standard quantification limits for the volatile priority pollutants are 5 $\mu\text{g L}^{-1}$ for ground water (8260C EPA Method 2006), 1 mL of water sample should contain at least 5 ng of each of the target analytes. Taking into consideration that the specification detection limit of the Pegasus GC-HRT (LECO, USA) mass spectrometer used in the present study is 1 pg of octafluoranthalene on column, even 1 μL of sample would be enough to detect and quantify reliably all the volatile priority pollutants at the required level. Although injection of water samples directly into GC column is possible, it is not typically done as it leads to the rapid deterioration of the column. Therefore, the required approach should involve quantitative transfer of all the organic constituents from a small water volume into an adequate volume of an organic solvent.

In the present study, 1 ml of water with standard additions of priority pollutants (1–100 ng) and 1 ml of dichloromethane as an extraction solvent were used. Anhydrous sodium sulfate as a reagent to bind water simultaneously improved the extraction due to the “salting-out” effect. This approach is widely used in classic liquid–liquid extraction for decreasing the solubility of organic compounds in water and increasing their extractability (Richardson et al. 2008). After addition of the sodium sulfate (~ 1.8 g), the aqueous phase was totally bound and the organic compounds were quantitatively transferred into the organic phase. Actually, the process may be considered as a replacement of the aqueous phase by the organic phase (dichloromethane in this experiment). All sampling procedures take 5–10 min, and there is no need to concentrate the sample. Therefore, there are no losses of volatile

components. Furthermore, *the sample preparation could be implemented completely outside the laboratory, in the field at any sampling site.*

The internal standard approach is based on the preliminary calculation of the response factors (RF) for each of the targeted analytes:

$$\text{RF} = \frac{S_{\text{is}} \times M_x}{S_x \times M_{\text{is}}}$$

where RF is response factor, M is amount of the compound in the standard solution, S is the signal intensity (peak area); index is refers to the internal standard, and index x refers to the analyte.

Table 1 represents the response factor values for the studied pollutants calculated as averaged results based on three injections at four concentrations (5, 10, 25, and 100 $\text{pg}/\mu\text{L}$).

$$\text{SD} = \sqrt{\frac{\sum_{i=1}^n (\text{RF}_i - \text{RF}_{\text{av}})^2}{n - 1}} \quad \text{RSD} = \frac{\text{SD}}{\text{RF}_{\text{av}}} \times 100\%$$

For all 47 targeted volatile compounds, RF values (Table 1) are situated in quite a narrow range between 0,22 (1,1,1,2-tetrachloroethane) and 3,6 (benzene). It allows for rather accurate quantitative measurements. Almost all of the relative standard deviations (RSD %) calculated using formulas 1 and 2 do not exceed 15 %, satisfying the requirements of the classic 8260C and 8270D EPA Methods. Only three compounds may be considered as exceptions. These were chloroform, 1,1,2,2-tetrachloroethane, and 1,2,3-trichloropropane (Table 1). Since the tendency for the variation of RF for these compounds was always the same (an increase in RF with the decrease in the concentration), it was natural to suppose that these compounds were present in the commercial dichloromethane used for the extraction. Calculations based on the results obtained and treating all the experiments as a version of the standard addition method allowed for quantification of these impurities. The results were as follows: chloroform— ~ 20 ng/mL, 1,1,2,2-tetrachloroethane—2 ng/mL, 1,2,3-trichloropropane—1 ng/mL. Taking into account these values, the RF figures for these compounds were recalculated. The corresponding figures are marked in Table 1 with superscript letter ‘a’. Therefore, dealing with these highly chlorinated volatile compounds, one should be cautious

Table 2 The recoveries (%) of 47 priority pollutants at four concentrations

Peak no.	Name	Recoveries (%) at four concentrations				Averaged recoveries	SD	RSD %
		5	10	25	100			
1	<i>cis</i> -1,2-Dichloroethylene	71	76	75	83	76	5.0	6.6
2	2,2-Dichloropropane	73	64	76	86	75	9.1	12.1
3	Bromochloromethane	81	89	90	90	88	4.4	5.0
4	Chloroform	99	99	88	90	93	5.7	6.1
5	1,1,1-Trichloroethane	64	60	74	83	70	10.3	14.7
6	1,2-Dichloroethane	91	95	90	89	95	8.3	8.7
7	1,1-Dichloropropene	86	72	75	72	78	7.0	9.0
8	Benzene	94	91	79	80	84	7.7	9.2
9	Carbon tetrachloride	68	66	65	76	69	5.0	7.2
10	Trichloroethylene	72	74	72	82	75	4.8	6.4
11	1,2-Dichloropropane	90	81	78	75	83	7.5	9.0
12	Dibromomethane	91	80	99	100	92	9.3	10.1
13	Bromodichloromethane	91	99	90	87	95	8.9	9.4
14	Toluene	97	85	78	74	87	11.1	12.8
15	1,1,2-Trichloroethane	68	87	94	97	87	13.0	14.9
16	1,3-Dichloropropane	82	92	94	91	90	5.3	5.9
17	Dibromochloromethane	76	91	98	99	91	10.6	11.6
18	Tetrachloroethylene	71	58	74	80	71	9.3	13.1
19	1,2-Dibromoethane	85	87	95	93	86	10.3	12.0
20	Chlorobenzene	70	77	82	84	78	6.2	7.9
21	1,1,1,2-Tetrachloroethane	70	75	91	93	82	11.5	14.0
22	Ethylbenzene	90	86	82	79	81	7.6	9.4
23	<i>m</i> + <i>p</i> Xylene	88	80	80	79	81	3.7	4.6
24	Bromoform	80	96	113	105	99	14.2	14.3
25	Styrene	74	80	84	79	79	4.1	5.2
26	<i>o</i> -Xylene	78	73	75	73	75	2.3	3.1
27	1,1,2,2-Tetrachloroethane	89	92	93	68	86	11.8	13.7
28	Isopropylbenzene	80	68	73	70	73	5.3	7.3
29	1,2,3-Trichloropropane	103	99	90	98	98	5.5	5.6
30	Bromobenzene	78	83	82	77	80	2.6	3.3
31	1-Chloro-2-methylbenzene	95	81	81	72	85	10.0	11.8
32	Propylbenzene	92	72	74	71	78	8.7	11.2
33	1-Chloro-4-methylbenzene	77	70	74	74	74	2.7	3.6
34	1,2,4-Trimethylbenzene	80	74	76	73	76	3.1	4.1
35	<i>tert</i> -Butylbenzene	75	80	78	76	77	1.9	2.5
36	1,2,3-Trimethylbenzene	76	73	79	72	75	3.2	4.3
37	1,3-Dichlorobenzene	67	76	90	86	80	10.3	12.9
38	<i>p</i> -Propyltoluene	82	71	76	73	76	4.8	6.3
39	1,4-Dichlorobenzene	68	79	87	84	80	8.3	10.4
40	<i>o</i> -Isopropyltoluene	70	73	76	72	73	2.5	3.4
41	1,2-Dichlorobenzene	78	83	88	87	84	4.5	5.4
42	Butylbenzene	78	81	84	75	79	3.4	4.3
43	1,2-Dibromo-3-chloropropane	81	89	110	110	98	14.8	15.0
44	1,2,4-Trichlorobenzene	67	81	96	89	83	12.4	14.9
45	Naphthalene	102	103	102	86	100	8.3	8.3
46	1,2,3-Trichlorobenzene	71	82	98	93	86	12.0	14.0
47	Hexachloro-1,3-butadiene	58	57	74	75	66	9.8	14.8

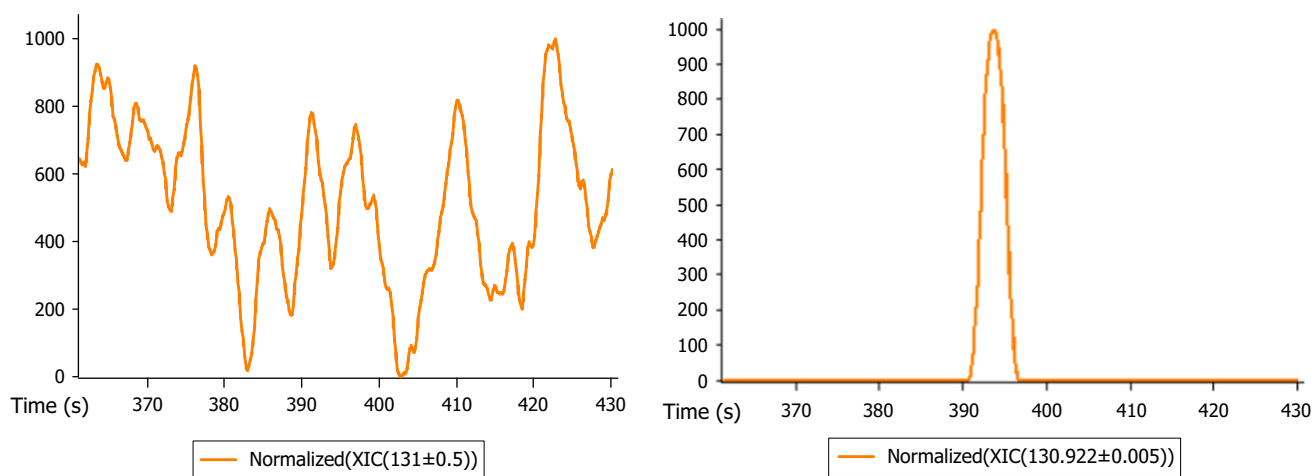


Fig. 1 Extracted ion current profiles using nominal mass (*left*) and accurate mass (3 decimal places) to detect 1,1,1,2-tetrachloroethane in a water sample

concerning the purity of dichloromethane. Alternatively, another solvent (e.g., MTBE) may be used.

The recoveries calculated for four concentrations are listed in Table 2. They are comparable with the recoveries of the standard US EPA 8260C (Method 8260C US EPA 2006), being quite reasonable for a reliable sensitive quantification. Only carbon tetrachloride and hexachlorobutadiene demonstrated averaged recoveries below 70 %. Another issue worth mentioning deals with the fact that several of the most volatile compounds (1,1-dichloroethylene, trans-1,2-dichloroethylene, 1,1-dichloroethane) are eluted earlier or together with dichloromethane and thus may be lost during the analysis. Obviously, dichloromethane itself cannot be measured using the proposed approach.

Another important issue worth special mentioning involves the importance of accurate mass measurements. According to the European Commission decision (2002/657/EC) (Eur. Union. 2002), a banned compound is considered “confirmed to be present in the sample” by GC/MS if the retention time is within the acceptance window and if the detection method provides four identification points. Since a measurement of the nominal mass provides 1 point, while a measurement of the high resolution/accurate mass provides 2 points, it is obvious that the application of high-resolution mass spectrometry (HRMS) is preferable. The recording of the accurate masses for 2 ions belonging to a certain compound allows this compound to be reliably identified (retention time should be considered as well). One peak (the most intense) is used for quantification and the second one for the identification confirmation. This issue becomes especially clear in the present study. Besides better reliability and elimination of the false-positive results (Polyakova et al. 2012, 2014), high-resolution/accurate mass measurements provide much better detection

limits, notably reducing the effect of background on quantification and simultaneously increasing signal-to-noise ratio (Polyakova et al. 2012; Lebedev et al. 2013). Figure 1 represents a rather dramatic case of the advantage of the high-resolution/accurate mass measurement in comparison with the nominal mass measurement for the detection of 1,1,1,2-tetrachloroethane.

Comparing the AWASP-GC/HRMS approach for the priority volatile pollutants with the most widely used for these compounds EPA Method 8260C, the following issues may be considered:

1. Sample preparation in the case of AWASP may be done directly in the field;
2. The requirements for the laboratory equipment and glassware are much lower for AWASP;
3. It is possible to automate AWASP;
4. It is potentially possible to expand the range of compounds amenable for the analysis working together with volatile and semivolatile compounds (Polyakova et al. 2014);
5. The results of HRMS based on accurate mass measurements are of higher reliability;
6. Due to the universality of the AWASP, this approach may be successfully used for non-targeted GC/MS analysis, when dealing with not preselected compounds;
7. AWASP is cheaper than EPA 8260C Method (2006).

Conclusion

The proposed AWASP sample preparation method for the GC/HRMS analysis of volatile priority pollutants in water samples is cheaper, faster, easier, and more reliable than

the existing sample preparation methods. It is also universal and able to expand the range of analytes, treating volatile and semivolatile compounds in one injection. Sample preparation may be carried out directly on site and may be automated.

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