

A static headspace GC-FID method for trace analysis of volatile organic compounds (VOCs) in waters

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The possibility of trace levels volatile organic compounds in water was investigated. Headspace was employed for isolation/preconcentration of the samples. Gas Chromatography with flame ionization detector followed. Some HS parameters were experimentally considered to maximizing the signal and sensitivity and minimizing the relative standard deviation of the results. Optimization of conditions was carried out using a lot of experiments combining different parameters. The optimized HS–GC–FID method was validated in terms of linearity, limit of detection, limit of quantitation and relative standard deviation.

Keywords: volatile organic compounds, gas chromatography, headspace

INTRODUCTION

Volatile organic compounds (VOCs) are organic chemical compounds that have high enough pressures under normal conditions to significantly vaporize and enter the atmosphere. Benzene, toluene, ethyl benzene, mixture of xylenes, isopropylbenzene and 4-ethyltoluene are among the volatile monoaromatic organic hydrocarbons found in petroleum derivatives [1]. Water contamination by monoaromatic compounds is a very serious problem as these compounds are toxic and classified as carcinogens for humans, especially benzene, which is a leukemic agent in humans and has a very low tolerance standard [2] and because they can change the taste and odour of drinking water. The chronic health effects to the general public from ingestion of VOCs at low concentrations in drinking water are less well understood but health values are well above offensive taste/odour thresholds and contain significant safety margins. The US environmental protection agency (EPA) has included these compounds on the list of national primary drinking water standards and established a maximum contaminant level (MCL) of 5.0 µg/L for benzene, for toluene 1000 µg/L, for ethyl benzene 700 µg/L and for xylenes 10,000 µg/L in drinking water [2, 3]. The presence of these compounds in both ground- and surface water are related to fuel spills, leaking underground storage tanks, and the release of unburned fuel directly into the atmosphere and surface waters [4, 5].

Analytical methods for investigation and determination of water contaminated with compounds of low concentrations is a complex problem that can be solved by using isolation and

pre-concentration procedures. VOCs concentration levels found in drinking and natural water samples are typically in the order of ng/L to µg/L. There are many techniques that can be used for the isolation and pre-concentration of the considered pollutants [6]. Conventional liquid-liquid extraction (LLE) [7], dispersive liquid-liquid microextraction [8], headspace (HS) techniques [9, 10], solid-phase extraction (SPE) [9, 11, 12] and solid-phase microextraction (SPME) [9, 12, 13] have all been used for isolation and pre-concentration of volatile organic compounds from water. Gas chromatography has commonly been used as a final step to obtain qualitative and quantitative results. The reason for this status is because chromatography combines the separation power of the method with the selectivity and sensitivity of detectors, able to fast qualitative and quantitative determination.

Head-space gas chromatography (HS-GC) indirectly determines the volatile constituent in liquid and solid samples by analyzing the vapor phased that is in thermodynamic equilibrium with the sample in a closed system. This technique is relatively simple and can provide sensitivity similar to dynamic purge and trap analysis. Complex sample matrices, which may be difficult to analyze directly or would require sample extraction or preparation can be placed in the vial with little or no preparation. Recently HS-GC is widely used in environmental analysis because of its advantages: economy of efforts and the attainment of a sample which is relatively free from the problems associated with the chromatographic properties of the matrix. As a gas extraction procedure it replaces a solvent extraction, thus avoiding the many problems with solvents.

Head-space extraction technique is classified into two types: static and dynamic. The theoretical

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Mustafa & Milina: A static headspace GC-FID method for trace analysis of volatile organic compounds (VOCs) in waters principles and quantification by two types headspace have been clearly described in several papers [14-17]. For routine analysis static headspace GC is the method of choice because it is rapid and requires no cleaning between samples while dynamic headspace is a much slower method because the sample tube and trapping column are difficult to clean and often require purging of the system to completely remove some volatile compounds.

It is known that different parameters affect headspace extraction. Optimization of this procedure requires consideration of parameters including vial equilibration time, extraction temperature and sample volume.

In this work possibility of trace levels volatile organic compounds in water was investigated. The influence of the different conditions for headspace analysis was investigated in order to reach low concentrations of the determinable compounds. A method using HS-GC-FID was validated.

EXPERIMENTAL

Chemicals and standard solutions

All chemicals used were of the highest available purity purchased from Sigma – Aldrich (Switzerland) and Supelco. A stock standard solution of benzene, toluene, ethylbenzene, o-xylene, p-xylene, iso-propylbenzene and 4-ethyltoluene was prepared in methanol. The vial was sealed, mixed and were stored in a refrigerator at 4°C. Working standard solutions of lower concentrations were prepared by dilution of the stock standard solution with deionized water to the required concentration.

GC analysis

GC analyses were carried out on a GC system Agilent Technologies 7890A equipped with flame ionization detector (FID) and split/splitless injector. The fused silica column used was HP-5, 30 m x 0.320 mm I.D. film thickness 0.25 µm. Temperature program of the oven: initial temperature 50°C for 2 minutes, rate 5 °C/min to 120°C, 2 minutes. Detector temperature: 300°C,

injector temperature: 250°C. Carrier gas: He, column flow 1.2 ml/min. Hydrogen flow 40 ml/min, air flow 400 ml/min, make-up gas (nitrogen) 40 ml/min. ChemStation for GC was used for instrument control, data acquisition and data analysis.

Static headspace GC analyses were carried out using Agilent 7694 Headspace Sampler.

Optimization

Different parameters that influence the extraction efficiency in a headspace experiment of the VOCs were optimized, selecting peak areas as response. Optimization of conditions was carried out using experiments combining 5 sample volumes in the headspace vial, 5 sample equilibration times and 4 temperatures of the oven and triplicate analyses.

RESULTS AND DISCUSSION

Optimization of Headspace parameters

The most important parameters affecting extraction efficiency in a headspace experiment are sample volume, sample equilibration time and temperature of the sample in oven [14].

Different parameters that influence the extraction efficiency in a headspace experiment of the VOCs were optimized. All parameters which may influence benzene, toluene, ethylbenzene, o-xylene, p-xylene, iso-propylbenzene and 4-ethyltoluene analysis are discussed below.

Selection of optimal sample volume

Headspace sample vials are typically in 10 ml and 20 ml sizes. We used 20 ml vials in order to have more possibilities to vary the sample weight.

The analytical chemist would increase the concentration of the sample or inject more samples onto a column to get a better signal. With headspace, more sample volume does not always provide the expected increase in peaks areas. We changed the sample volume from 5 to 16 ml at two different temperatures but the same time. Five samples with analytes concentration (160 µg/l) and sample volumes: 5, 10, 12, 14 and 16 ml were investigated. The other parameters were sample equilibration time 15 minutes, oven temperature 75°C and 85°C.

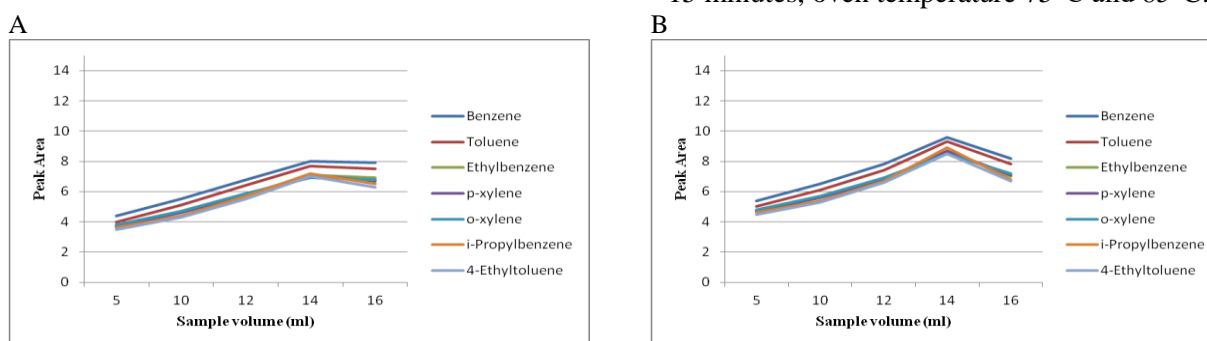
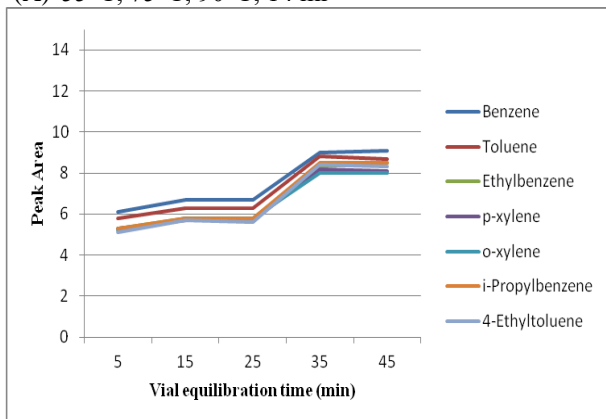
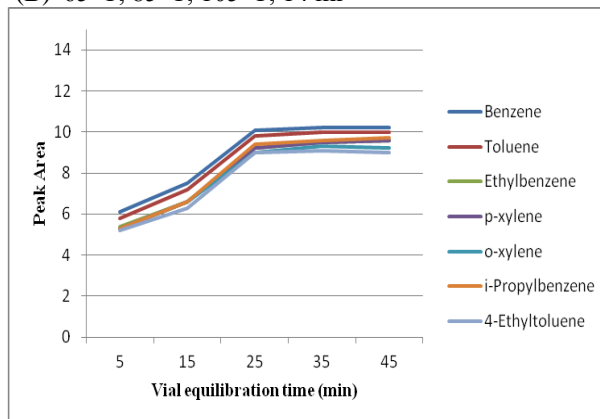


Fig. 1 The effect of sample volume on a detector response (peak area) of the VOCs. Extraction conditions: analytes concentration 160µg/L, sample equilibration time 15 minutes, oven temperature 75°C (A) and 85°C (B).

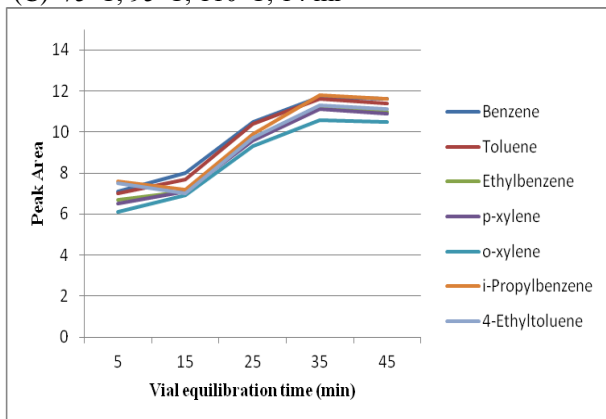
(A) 55°C, 75°C, 90°C, 14 ml



(B) 65°C, 85°C, 105°C, 14 ml



(C) 75°C, 95°C, 110°C, 14 ml



(D) 85°C, 100°C, 120°C, 14 ml

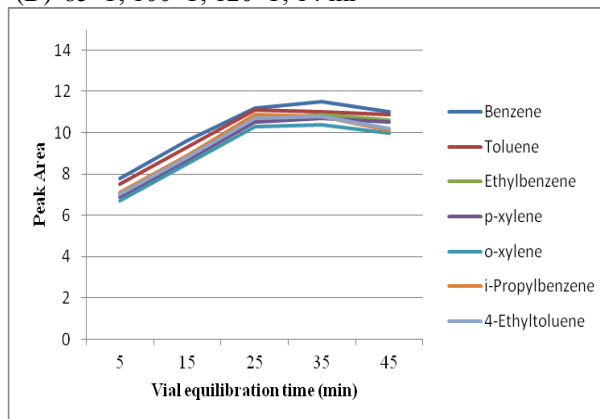


Fig. 2 The effect of sample equilibration time and temperature on a detector response (peak area) of the VOCs. Extraction conditions: analyte concentration 160 μ g/L, sample equilibration time 5 – 45 minutes, oven temperature 55°C (A), 65°C (B), 75°C (C), 85°C (D).

The results shown in Fig.1 A and B indicates that for all analytes the analytical signal increases with sample volume in the range of 5–14 ml and after 14 ml the rate of increase slows down (75°C) or even decreases (85°C). Hence, a sample volume of 14 ml was applied to subsequent experiments.

Selection of Sample equilibration time and temperature

Other two factors that should be considered at this point are the equilibration time and temperature. Higher temperatures lead to higher vapor pressure of the analyte and hence its concentration in the headspace increases. The effect of temperature and time on the extraction was investigated at 4 different temperatures 55°C, 65°C, 75°C, 85°C for five different equilibration times 5, 15, 25, 35 and 45 min respectively. It was not possible to apply a higher temperature than 85°C because would be introduced a higher amount of water (as vapor) during the headspace injection and this would lead to an increase in background level.

As shown in Fig. 2 the highest detector response was obtained when the thermostat was kept at 75°C (C) and 85°C (D), but the equilibration time at 75°C

was ten minutes longer. It can be also seen that the difference in detector response between the lowest (55°C) (A) and the highest (85°C) (D) temperature is two orders of magnitude. Therefore, an equilibration time of 25 min and equilibration temperature of 85°C were selected for further experiments.

Method validation

After analyzing all experimental results, the following conditions have been selected to evaluate the performance of the method: 14 ml water samples, equilibration time of 25 min and equilibration (oven) temperature 85°C. The method of external standard was used for quantitation.

Typical validation characteristics which should be considered are Accuracy, Precision (Repeatability, Intermediate Precision), Specificity, Limit of detection (LOD), Limit of quantitation (LOQ), Linearity, Range [18-20].

The optimized HS-GC-FID method was validated in terms of linearity, precision, limit of detection (LOD), limit of quantitation (LOQ) and relative standard deviation RSD (%).

To evaluate the linearity of the method, a calibration curve was performed with working aqueous standards containing concentrations in the range from 5 - 200 µg/L for all analytes. Three replicate samples for each point were made. The calibration curve constructed was evaluated by its correlation coefficient. All the analytes exhibited good linearity over the range studied with correlation coefficients (r^2) between 0.9951 and 0.9974 (Table 1).

LOD of an analytical method refers to the lowest amount of analyte that can be detected which is not necessarily quantified as an exact value. Meanwhile, LOQ is the lowest concentration of an analyte that can be quantitatively determined with appropriate precision. In a GC measurement, both LOD and LOQ are important. The LOD and LOQ were

calculated as 3 SD and 10 SD respectively [18-21]. The results obtained are show Table 1.

Precision as relative standard deviation RSD (%) and accuracy as recovery (%) were measured by spiking the sample with two known concentrations (5 and 100 µg/L) of each aromatic hydrocarbon. The spiked sample was analyzed five times following the described procedure.

The spiked concentrations and standard deviation values for the precision and accuracy also are given in Table 1. For five independent determinations at 5 and 100 µg/L, precision (RSD) was between 4.90 % to 9.13 % for the low level and 1.80 % to 4.71 % for the high level. Accuracy from spiked water was between 79.41 and 98.82 % for the low level and 93.00 and 99.98 % for the high level.

Table 1. Parameters of calibration curves for investigated VOCs in water, precision, accuracy results for the analysis of VOCs in spiked water, LOD and LOQ

Compound	Linear range (µg/L)	Correlation coefficient (r^2)	Spiked Conc. (µg/L)	RSD (%)	Accuracy (%)	LOD µg/L	LOQ µg/L																																																													
Benzene	5.19 – 207.60	0.9958	5.19	6.57	93.83	0.96	3.20																																																													
			96.90	2.31	99.98			Toluene	5.13 – 205.20	0.9964	5.13	6.80	93.90	0.96	3.20	95.80	2.04	99.50	Ethylbenzene	5.13 – 205.20	0.9967	5.13	4.90	95.51	0.72	2.40	95.80	1.80	97.34	p-xylene	5.10 – 204.00	0.9966	5.10	6.76	95.68	0.99	3.30	95.20	2.97	99.02	o-xylene	5.22 – 208.80	0.9970	5.22	7.54	98.82	1.14	3.80	97.50	2.96	97.10	iso-Propylbenzene	5.10 – 204.00	0.9974	5.10	9.13	79.41	1.11	3.70	95.20	4.71	93.50	4-Ethyltoluene	5.10 – 204.00	0.9951	5.10	8.40	79.60
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CONCLUSIONS

The possibility of trace levels volatile organic compounds in water using static head-space was investigated. Capillary gas chromatography with flame ionization detector was used for resolution and quantitation. The most important parameters affecting extraction efficiency in a headspace experiment of the VOCs were optimized. The optimized HS-GC-FID method was validated in terms of linearity, limit of detection (LOD), limit of quantitation (LOQ) and relative standard deviation RSD (%). All the analytes exhibited good linearity over the range studied (5 - 200 µg/L) with correlation coefficients (r^2) between 0.9951 and 0.9974. LODs and LOQs varied from 0.72 to 1.14 µg/L and from 2.4 to 3.8 µg/L, respectively.

REFERENCES

1. A. Sarafraz-Yazdi, A. Amiri, Z. Eshaghi, *Chemosphere*, **71**, 671 (2008).
2. Y. AlSalka, F. Karabet, S. Hashem, *Anal. Methods*, **2**, 1026, (2010).
3. USEPA, List of Contaminants & their Maximum Contaminant Level (MCLs) in drinking water, <http://www.epa.gov/safewater/mcl.html#organ ic>.
4. I. Arambarri, M. Lasa, R. Garcia, E. Millan, *J. Chromatography A*, **1033**, 193 (2004).
5. M. Rosell, S. Lacorte, A. Ginebreda, D. Barcelo, *Journal of Chromatography A*, **995**, 171 (2003).
6. K. Demeestere, J. Dewulf, B. De Witte, H. Van Langenhove, *J. Chromatography A*, **1153**, 130 (2007).
7. D. Peroni, W. Egmond, W. Kok, H. Janssen, *J. Chromatography A*, **1226**, 77 (2012).
8. Y. Assadi, F. Ahmadi, M. Reza, M. Hossieni, *Chromatographia*, **71**, 1137 (2010).

9. J. Menendez, M. Sanchez, J. Uria, E. Martinez, A. Sanz-Medel, *Anal. Chim. Acta*, **415**, 9 (2000).
10. A. Serrano, M. Gallego, *Journal of Chromatography A*, **1045**, 181 (2004).
11. C. Erger, T. Schmidt, *Trends Anal. Chem.*, **61**, 74 (2014).
12. P. Castells, F.J. Santos, M.T. Galceran, *J. Chromatography A*, **1025**, 157 (2004).
13. H. Piri-Moghadam, F. Ahmadi, J. Pawliszyn, *Trends Anal. Chem.* **85**, 133 (2016).
14. A.C.Soria, M.J.Garcia-Sarrio, M.L.Sanz, *Trends Anal. Chem.* **71**, 85 (2015).
15. C. Bicchi, C. Cordero, E. Liberto, B. Sgorbini, P. Rubiolo, *J. Chromatography A*, **1184**, 220 (2008).
16. N.H. Snow, G.P. Bullock, *J. Chromatography A*, **1217**, 2726 (2010).
17. B. Kolb, *J. Chromatography A*, **842**, 163, (1999).
18. I. Taverniers, M. De Loose, E. Van Bockstaele, *Trends Anal. Chem.*, **23**, 535 (2004).
19. B. Magnusson, U. Örnemark (eds.) Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics, (2nd ed. 2014).
20. ICH-Q2A, Guideline for Industry: Text on Validation of Analytical Procedures, 1995.
21. A. Shrivastava, V. Gupta, *Chron. Young Sci.*, **2**, 21 (2011).