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Contemporaneous Determination of Multiple Volatile Organic Compounds (VOC) in Aqueous Solution Using a Novel Static Headspace GC-MS Method

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Abstract

Chlorinated solvents are a class of organo-halogen compounds widely spread in the environment. These volatile organic compounds (VOCs) are also the most common cause of water contamination in the U.S. and Europe. All chlorinated solvents are toxic and irritating and represent a serious health concern to individuals. To simultaneously assess the greatest number of analytes, we devised and validated a novel analytical method for quantitative determination of VOCs using a static headspace SHS-GC-MS analysis. Our method allowed for the determination of multiple analytes in few minutes, the reduction of analytical cost per sample, and an increase of efficiency. To further refine the instrument calibration and more accurately prepare the analytical standards, chemometric analysis is recommended.

Introduction

Chlorinated solvents are a class of organo-halogen compounds widely spread in the environment. These compounds are widespread and represent also the most common cause of water contamination in the U.S. and Europe. All chlorinated solvents are toxic and irritating and constitute a serious concern to individuals because of their proven carcinogenicity (1). Being volatile these substances can contaminate surface water mainly in the proximity of the spill sites. These compounds also affect aquifers because of their higher density respect to water.
Therefore, in order to simultaneously assess the greatest number of analytes with a straightforward method, we devised and validated a novel analytical method. Our method allow for a quantitative determination of up to 30 volatile organic compounds (VOCs) using a static headspace SHS-GC-MS analysis in just only 15 minutes. Moreover, this method has a higher sensitivity and lower limits of detection (LOD) and quantitation (LOQ) respect to already standardized techniques (2,3) or methods employing more sophisticated instrumentation (4).
In conclusion, our method allows for the determination of multiple analytes in few minutes, the reduction of analytical cost per sample, and an increase of efficiency. To further refine the instrument calibration employing and more accurately prepared analytical standard solution, a chemometric approach is further recommended.

Materials & Methods

Standard solution preparation

The standard solution employed in our study was prepared from a 100 μg/ml stock solution in methanol (Supelco analytical, EPA 624 calibration Mix 1, catalog no. 47506) of the following analytes: Chloromethane, Vinyl chloride, Bromomethane, Chloroethane, Trichlorofluoromethane, 1,1-Dichloroethylene, Dichloromethane, trans-1,2-Dichloroethylene, 1,1-Dichloroethane, Chloroform, 1,1,1-Trichloroethane, Carbon tetrachloride, Benzene, 1,2-Dichloroethane, Trichloroethylene, 1,2-Dichloropropane, Bromodichloromethane, cis-1,3-Dichloropropene, Toluene, trans-1,3-Dichloropropene, 1,1,2-Trichloroethane, Tetrachloroethylene, Dibromochloromethane, Chlorobenzene, Ethylbenzene, 1,1,2,2-Tetrachloroethane, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene and 1,2-Dichlorobenzene.

All of the analytes were analyzed in Selected Ion Storage (SIS) mode, taking into account the target ion and several m/z characteristic values in static head-space mode. The Limit of Detection (LOD) ranges between 0.14 and 0.01 ppb and Limit of Quantitation (LOQ) ranges between 0.60 and 0.03 ppb.

SHS-GC-MS method

For each analytical determination 20 ml vials for head-space use were filled with 10 ml of deionized water and the misture of VOCs were added to it. Samples were placed in an autosampler and subjected to analysis. We employed a Varian 431 GC system couplet with a Varian 210 mass spectrometric detector. The employed column was a DB-624 (Agilent) suited for chlorinated molecules analysis. Most of the analytes were separated with a programmed temperature. The autosampler was a QUMA QHSS with 50 places. The instrumental parameters were as follows: 1) SHS: incubation 15 min 80°C shake mode; 2) GC: Inlet Split/Splitless 180°C, split 1/15, headspace liner, Column: VB-624, 30m x 0,25 mm x 1μm. Gas: He, constant pressure, Oven: 35°C (2 min), 50°C at 6 °C/min, 180°C at 12°C/min, Run time: 15 min, Flow: 1 ml/min; 3) MS: Transfer line: 180°C, Manifold: 80°C, Ion source: 150°C
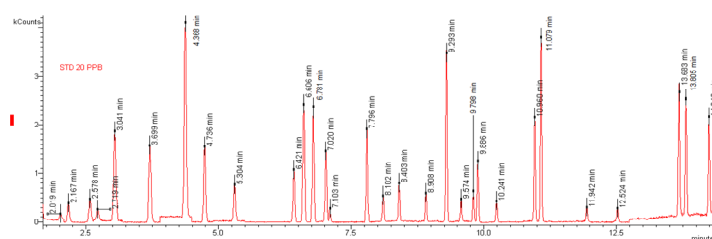

Figure 1. GC profile of the standard solution of VOCs.

Results

Figure 1 shows the chromatogram of a standard solution obtained with our method. The 30 analytes present a good separation and are clearly distinguishable. Integration was possible also for the most diluted samples. Four analytes were determined with the lowest LOD (0.01 ppb) and most of them have a LOD<0.1 ppb. Only four of them were determined with a LOD>0.1 ppb.

The method was therefore validated using "real samples" consisting in two aqueous samples coming form different polluted sites.

Table 1 reports the analytes determined in several polluted sites.

Conclusions

Our method allowed the determination of up to 30 VOCs in just only 15 minutes with a higher sensitivity. The analytical cost per sample and an increase in efficiency has to be expected by implementing this method in the laboratory routine. To further refine the instrument calibration a chemometric approach should be devised and applied.

Table 1. VOCs determination in several polluted sites

Analyte	Sample 1 (ppb)	Sample 2 (ppb)	Sample 3 (ppb)	Sample 4 (ppb)	Sample 5 (ppb)	Sample 6 (ppb)	Sample 7 (ppb)
Vinyl chloride	- - -	15.5	- - -	- - -	- - -	- - -	- - -
Chloroform	- - -	- - -	- - -	- - -	- - -	5.9	3.8
1,1,1-Trichloroethane	- - -	- - -	- - -	1.9	- - -	- - -	- - -
Benzene	4.7	3.8	4.4	6.0	5.8	2.2	- - -
1,2-Dichloroethane	1.8	- - -	- - -	- - -	- - -	- - -	- - -
1,2-Dichloropropane	- - -	2.0	- - -	- - -	- - -	- - -	- - -
Bromodichloromethane	- - -	2.7	- - -	- - -	- - -	- - -	- - -
Toluene	2.5	22.2	1.5	1.7	2.4	3.1	2.3
Chlorobenzene	- - -	- - -	- - -	- - -	2.4	- - -	- - -
Ethylbenzene	- - -	21.1	- - -	2.1	2	- - -	1.6
1,4-Dichlorobenzene	7.4	25.5	1.9	15.5	- - -	- - -	- - -

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