Available online at www.sciencedirect.com
ScienceDirect
Journal of Hazardous Materials 145 (2007) 336–338
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Short communication

Evaluation of Microwave-Assisted Process technology for HAPSITE's headspace analysis of volatile organic compounds (VOCs)

Jacqueline M.R. Bélanger [a,*], J.R. Jocelyn Paré [a], Rodney Turpin [b], Joe Schaefer [b], C.W. Chuang [c]

[a] *Environment Canada, Green Technologies Division, 335 River Road, Ottawa, Ont., Canada K1A 0H3*
[b] *US EPA, Emergencies Response Team, 2890 Woodbridge Ave., Edison, NJ 8837-3679, USA*
[c] *Lockheed Martin/REAC, 2890 Woodbridge Ave., Edison, NJ 08837, USA*

Received 25 July 2006; received in revised form 6 December 2006; accepted 19 December 2006
Available online 8 January 2007

Abstract

The use of microwave energy as a heating source for the field-based headspace sampling and the subsequent determination of various volatile organic compounds (VOCs) using a field-portable HAPSITE gas chromatograph–mass spectrometer has been evaluated. A significant advantage in time reduction has been observed when using microwave energy when compared to conventional resistive-based heating. Such time savings are critical in field operations involving equipment such as the HAPSITE where non-routine sampling is commonly performed and very quick turnaround time is usually needed. Further, the technology also showed significant improvements in terms of sensitivity, thus suggesting its applicability to a broader range of compounds and detection levels than current technologies.

Keywords: Microwave-Assisted Process (MAP); Microwave energy; Headspace analysis; HAPSITE; Volatile organic compounds (VOCs) analysis

1. Introduction

There is always a need for new person-portable equipment that could be used by first responders as analytical tools for early, fast, and precise determination of chemicals at emergency response sites.

Recently, we have introduced a microwave apparatus as an alternative for generating headspace at great efficiency in less than 2 min (a technology within the Microwave-Assisted Processes (MAP™[1]) technologies). We evaluated the use of this microwave prototype by comparing analysis results of headspace samples generated between the HS and the microwave apparatus. It was concluded that the use of microwaves as an energy source for the generation of volatiles provided significant benefits in terms of incubation time and sensitivity [1–5]. While the former is not truly an issue in routine laboratory analysis where commercial apparatus make use of several incubation chambers simultaneously, it is a vital element for field-based analysis. When we combine this short incubation time to the no thermal inertia conditions inherent to microwaves, we obtain the potential for significant improvement to current field-based analysis, be it in vehicle-portable or person-portable apparatus. Changing "temperature" conditions is in fact instantaneous.

In our continuing studies toward the development of field-portable analytical equipment we are now reporting on the evaluation of the interfacing and use of MAP for a HAPSITE's portable gas chromatograph–mass spectrometer analysis system for volatile organic compounds (VOCs) in water and in soil samples. The latter has been subject to several critical validation and review studies [6–12].

2. Experimental

The VOCs used for the evaluation are presented in Table 1. The concentration of each compound used in the analysis was 50 μg/L and each sample was done in triplicate.

At preset, HAPSITE portable GC-MS is interfaced with a headspace sampling unit (HS) for analysis of VOCs in water

* Corresponding author. Tel.: +1 613 990 9239; fax: +1 613 990 2855.
E-mail address: Jacqueline.Belanger@ec.gc.ca (J.M.R. Bélanger).

[1] MAP is a Trade-Mark of Her Majesty the Queen in Right of Canada as represented by the Minister of the Environment.

0304-3894/$ – see front matter.
doi:10.1016/j.jhazmat.2006.12.074

Table 1
Volatile organic compounds used (50 μg/L of each compound)

Internal standard	Surrogate	Analyte
Dibromofluoromethane	1,2-Dichloroethane-*d*4	1,1-Dichloroethene
Fluorobenzene	Toluene-*d*8	Benzene
Chlorobenzene-*d*5	1,4-Dichlorobenzene-*d*4	Trichloroethene
4-Bromofluorobenzene		Chlorobenzene toluene

Fig. 1. Photograph presenting a typical instrument layout in a field laboratory. The pictured HAPSITE GC–MS sits at the centre and is equipped with conventional headspace (left) and MAP-HS apparatus (right). The current MAP-HS configuration is not specific to HAPSITE and it is operated via a remote controller (that is located on top of the MAP-HS in this picture).

and soil samples. The HS employs a regular heating element to heat a 40 mL glass vial (with 20 mL aqueous solution) at 60 °C for a minimum of 20 min before the headspace is being injected into the HAPSITE for subsequent analysis.

Microwave-assisted headspace sample generation was carried out in a Soxwave-10 atmospheric pressure focused extraction system (Prolabo, Fontenay-Sous-Bois, France). It was made up of one command box and one microwave cavity modules. Our system operates at a fixed frequency of 2450 MHz and was capable to emit continuously variable power output of 20–200 W in 10 W increments. Conventional HAPSITE 20-mL vials were used as is and inserted directly into the sample compartment. Typical conditions used were set at a power of 100 W for a cycle of 20 s ON, 10 s cooling time, 20 s ON. The sample was then transferred into the regular HAPSITE HS apparatus and injected without any delay. This approach allowed avoiding any variation associated with sample transfer so that sensitivity was only affected by the volatile generation techniques under study.

Fig. 1 is a photograph that depicts a typical instrumental layout in a field laboratory as used in the performance of this work.

3. Results and discussion

Table 2 presents the peak response obtained from the HAPSITE GC–MS as well as the sampling conditions. The data were

Table 2
Peak response of each target analyte

Analytes	MAP	HAPSITE 20-mL vial	HAPSITE 40-mL vial
Dibromofluoromethane	1.48	1.0	1.52
Fluorobenzene	1.53	1.0	1.60
Chlorobenzene-*d*5	1.44	1.0	1.63
4-Bromofluorobenzene	1.80	1.0	1.62
1,2-Dichloroethane-*d*4	1.59	1.0	1.41
Toluene-*d*8	1.56	1.0	1.60
1,4-Dichlorobenzene-*d*4	1.66	1.0	1.48
1,1-Dichloroethene	1.37	1.0	1.68
Benzene	1.57	1.0	1.56
Trichloroethene	1.32	1.0	1.63
Toluene	1.52	1.0	1.63
Chlorobenzene	1.46	1.0	1.60

HS sampling
Microwave operated at 100 W (50% of nominal power)
Irradiation sequence: 20 s ON–10 s OFF–20 s ON
Conventional heating: 60 °C for 20 min

Average of three measurements, normalized for 20-mL HAPSITE data. Overall relative standard deviation for MAP of 5.8%, for HAPSITE 20-mL vial of 5.7% and for HAPSITE 40-mL vial of 2.1%.

normalized against the response obtained when using 20-mL vials and the HAPSITE conventional heating source for 20 min at 60 °C. These preliminary, non-optimized, results show that microwave-assisted heating in 20-mL vial generates equivalent peak response as the regular 40-mL vial in the HS. These results suggest that microwave-assisted heating can be considered an alternative for headspace analysis offering significant time savings (*i.e.*, 50 s *versus* 20 min) while generating quantifiable and reproducible data. The advantage of such time reduction would be critical in field operations involving equipment such as the HAPSITE where non-routine sampling is commonly performed and very quick turnaround time is usually needed.

As demonstrated in this paper, there is a significant advantage in time reduction when using microwave energy to perform headspace analysis of volatile organic compounds. Such time savings are critical in field operations involving equipment such as the HAPSITE where non-routine sampling is commonly performed and very quick turnaround time is usually needed.

With further refinement of the microwave-generating apparatus, especially in the area of weight reductions made possible with the advent of solid-state generators capable of over 100 W, this technology offers significant potential as an alternative to conventional resistive heating HS for field operations. Further, it is anticipated that ancillary technologies such as the injection mechanism, the transfer line, and the dc power capability, can be used with minor modifications if any.

The advent of solid-state technology capable of hundreds of watts raised the potential to apply the MAP-headspace technology to field-based work. Until they are readily available, it is timely to assess the potential of the technology using well-proven magnetron based single-mode focused microwave apparatus. The coupling of MAP-HS technology to portable field analyzer such as a HAPSITE headspace apparatus for the analysis for volatile organic compounds (VOCs) in water and in soil

samples is especially appealing as the technology promises to be much faster than what is available now in addition to offer significant sensitivity enhancements as a result of the better and higher heating made possible by the use of the MAP technology.

Safety disclaimer

These experiments were carried out by highly skilled personnel well abreast of risks and hazards associated with subjecting volatilised materials to microwave energy while within a confined volume. Special care should be exercised if and when attempting to reproduce the present work. This hazard level will be reduced, if not totally removed, when commercial instrumentation is made available to the laboratory community. By the same token, when such instrumentation is available, even higher sensitivity will be achieved as the containers used therefore will have been designed specifically for that purpose.

Despite the seemingly simple nature of the procedure reported herein, workers should refrain from using domestic microwave ovens. The wide availability of such non-laboratory approved equipment makes it tempting but at no time should the safety of operators be overlooked, and extreme care should be exercised as a result of the inherent danger of explosion. For example, using the procedure described above, the surface temperature of the HS vial was measured to be above 110 °C and the pressure up to above 12 psi. There should be no vigorous boiling or excessive distortion of the septum seal. The tab at the centre of the safety cap is designed to peel back by the bulging septum if the pressure limit is exceeded. During the microwave exposure period, interrupt the power application immediately upon hearing any knocking or bumping noise, which may be indicative of imminent release of excessive pressure. In handling the vial after irradiation, use tongs with long handles and always wear proper face protection in the form of a clear face shield with an apron to protect the neck area.

Commercially available domestic ovens have so-called "duty cycles" (i.e., the magnetron is not always ON), hence making it possible to give rise to rapid increases in pressure and enhance considerably the risk of explosion. This characteristic of domestic ovens also has the effect of reducing significantly the level of reproducibility.

References

[1] J.R.J. Paré, U.S. Patents 5,377,426 (1995); 5,519,947 (1996); 5,675,909 (1997); 5,732,476 (1998); 5,884,417 (1999).
[2] J.R.J. Paré, J.M.R. Bélanger, S.S. Stafford, Microwave-Assisted Process (MAP™): a new tool for the analytical laboratory, Trends Anal. Chem. 13 (4) (1994) 176.
[3] J.R.J. Paré, J.M.R. Bélanger, K. Li, S.S. Stafford, Microwave-Assisted Process (MAP™): application to the headspace analysis of VOCs in water, J. Microcolum Sep. 7 (1995) 37–40.
[4] J.R.J. Paré, J.M.R. Bélanger, D.E. Thornton, K. Li, M. Llompart, M. Fingas, S.A. Blenkinsopp, Gas-phase extraction using the Microwave-Assisted Process (MAP™) for the analysis of dissolved volatile organic compounds (VOCs) in water, Spectrosc. Int. J. 13 (1996) 23–32.
[5] J.R.J. Paré, K. Li, J.M.R. Bélanger, M. Llompart, Gas-phase extraction method using the Microwave-Assisted Process (MAP™) for the determination of aromatic contaminants in soil, Spectrosc. Int. J. 13 (1996) 89–98.
[6] INFICON Technical Note diba84a1-c, HAPSITE Chemical Identification System, 2004.
[7] INFICON Technical Note no. diba84a1-a, HAPSITE Headspace Sampling System, 2003.
[8] US EPA Report No. EPA/600/R-98/142, Environmental Technology Verification Report, Field-Portable Gas Chromatograph/Mass Spectrometer, Inficon, Inc., HAPSITE, November 1998.
[9] US EPA Report No. EPA 542-R-01-011, Innovations in Site Characterization, Technology Evaluation: Real-Time VOC Analysis Using a Field Portable GC/MS, August 2001.
[10] C. Crume, Analysis of volatile organics by field-portable GC/MS, Environ. Test. Anal. (May/June) (2001) 25–26.
[11] B.A. Eckenrode, Environmental and forensics applications of field-portable GC/MS: an overview, J. Am. Soc. Mass Spectrom. 12 (2001) 682–693.
[12] S.P. Schuetz, P.J. Solinske, D.B. Mickunas, A.M. Humphrey, R.D. Turpin, Comparison of data quality produced by an on-site field GC/MS and off-site permanent laboratory GC/MS: support of cleanup action at an inactive drum recycling facility, J. Hazard. Mater. 43 (1995) 67075.