CAF

Current analytical advances in fumigation science at USDA-ARS

S S WALSE[1*], R L JIMENEZ[1], W A HALL[2]

[1]USDA, Agricultural Research Service, San Joaquin Valley Agricultural Sciences Center, 9611 S . Riverbend Avenue, Parlier, California, USA, 93648-9757

ABSTRACT

Recent work to improve analytical methodology for the detection of fumigants in the gas, or solid/liquid phase will be summarized. A barrier ion-discharge detector (BID) quantitatively detected fumigant gasses in concentrations ranging over several orders of magnitude. Head space analysis using either solid-phase micro extraction or a head space auto sampler equipped with an adsorbent trap accurately quantified fumigant residues in foodstuffs without lengthy sample preparation or the use of solvents. Normal atmospheric pressure mass spectrometers are discussed in the context of their use to quantify the depuration potential of fumigants for worker exposure evaluations. Detailed here is research related to the use of solid-phase micro extraction (SPME) to quantify methyl bromide (MB) concentrations in airs treams, and more specifically, effluent from the ventilation of post harvest chamber fumigations. Two SPME sampling techniques were investigated, direct fibre exposure (DFE) as well as time-weighted averaging (TWA), and results from compulsory experiments designed to probe and characterize MB quantification using the respective techniques are presented and discussed. Results support the use of TWA sampling for MB over the timescale of hours in airs teams containing up to 16,000 ppmv. The TWA sampling of MB was quantitative across the range of fumigation-relevant conditions, statistically unaffected by relative humidity, and had a limit of detection (LOD) of approximately 14 ng when coupled to gas chromatographic analysis with flame ionization detection (GC-FID).

Keywords: Food security, Food safety, Gas detection, Quantification and Worker safety

Methyl bromide (MB) is a highly effective postharvest fumigant with an approximate 50-year history of controlling insects and microorganisms across a wide variety of applications (e.g. foodstuffs, wood, etc.) (Bell et al., 1997; Johnson et al., 2012). It is an atmospheric source of reactive bromine gases (Lary, 1996), which deplete stratospheric ozone (Yung et al., 1980; Solomon, 1990). Anthropogenic utilization of MB is regulated by international agreement under the Montreal Protocol. In instances where post-harvest chamber fumigations are permitted, contribution(s) to ozone depletion can be minimized, or eliminated, by removing MB from the ventilation effluent via activated carbon or some other type of sorbent material (Leesch et al., 2000). Towards that end, it is necessary to assess the potential of sorbent materials to remove MB from airstreams.

An experimental apparatus, termed a parallel adsorbent column tester (PACT), was constructed as a scaled-down model of a chamber ventilation system material (Leesch et al., 2000). The PACT was used to evaluate, in parallel, gram-scale quantities of materials for capture performance, as a function of effluent flows (ca. 0 to 225 mL min^{-1}), volumes ($\geq$ 6.75 L), durations ($\geq$ 30 min), and [MB]'s (ca. 3 to 16,000 ppmv). Over the range of these conditions, solid-phase micro extraction (SPME) fibres have the potential to more effective than established methods for MB quantification (e.g. calorimetric tubes, gas-sampling, IR detection, electrochemical detection). Quantitative models for two SPME sampling techniques, direct fibre exposure (DFE) and time-weighted averaging (TWA) were applied to studies that explored the accuracy, precision, and reproducibility of using the DFE and TWA techniques to sample MB in the PACT system with flowing air, as well as in a static system

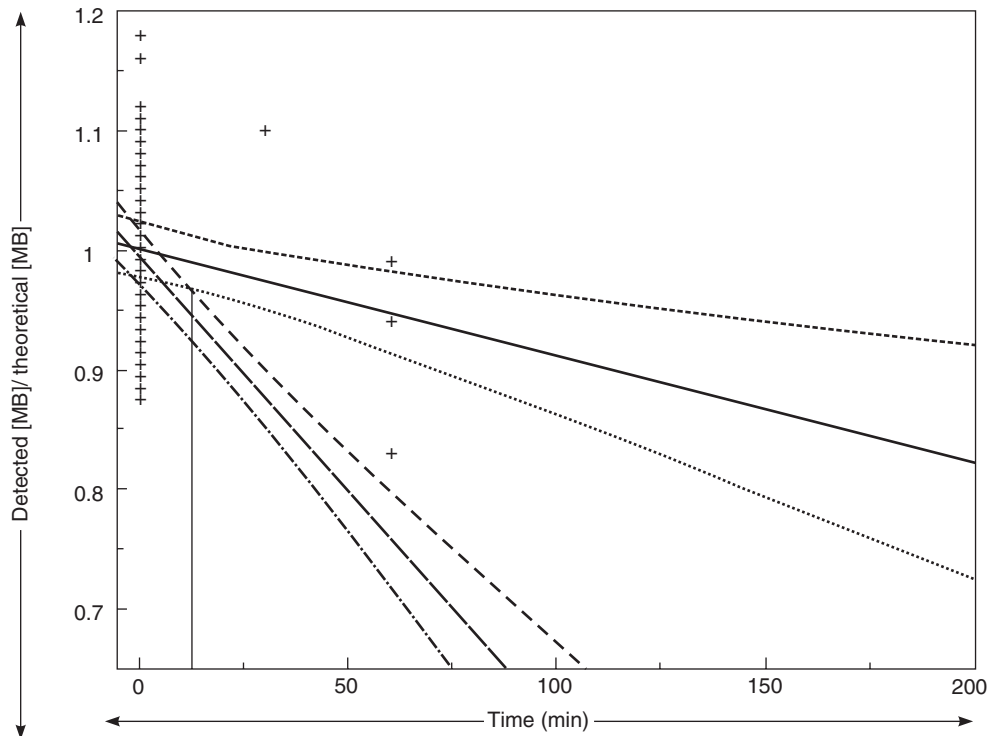[1]Corresponding author email: *spencer.walse@ars.usda.gov*

Fig. 1. Methyl bromide concentration ([MB]) detected relative to that expected with (solid line) or without (dashed line) burying the SPME fibre into a septum for varying durations (i.e. hold times) (min) prior to GC-FID analysis; dotted lines represent the 95% confidence intervals. Each point represents a trial conducted with a single fibre. Without burying the fibre into a septum, a statistically significant loss (95% confidence interval) of MB occurred after −11 min (solid vertical line), consistent with a 0.4% loss of MB/min

for comparison. We report results from compulsory experiments and discuss the potential for SPME-based sampling techniques to quantify MB in effluent from postharvest chamber fumigations.

MATERIALS AND METHODS

Modeling experimental details are as reported by Hall et al. (2015).

RESULTS AND DISCUSSION

SPME use with PACT: Time-weighted averaging (TWA) versus Direct fibre exposure (DFE) sampling. The effect of the airstream flow rate on the quantification of MB in the PACT system was evaluated. Airflows of 75 mL min^{-1} or 224 mL min^{-1} were established as the outlet flow from each channel of the PACT system with [MB]s metered to 5,092 ppmv or 548 ppmv for TWA and DFE sampling respectively. For both sampling approaches, a T-test showed no difference at the 99% confidence interval between MB quantification at either flow rate

(TWA, T-test: $t_4 = 0.7436$, $P > |t| = 0.5023$; DFE, T-test: $t_6 = 0.6214$, $P > |t| = 0.5680$).

However, if the simulated ventilation of a postharvest chamber fumigation is sampled using the TWA technique with a t of 30 min, an average [MB] of 3,434 ± 211 ppmv ($n = 35$, $\bar{x} \pm s$) (5 replicate analyses of 7 samplings) was obtained, which agrees well with a calculated [MB] of 3,731 ppmv. It is interesting to note that the accuracy of TWA sampling for MB quantification in the PACT system despite changes in concentration over the sampling interval, a period where no MB is released, and a relatively short exposure to the highest [MB]. This result is in marked contrast to DFE sampling in the PACT system with a single fiber (i.e., without temporally exchanging fiber assemblies) and $t = 30$ min, where m would be based overwhelmingly on the [MB] in the minutes preceding the conclusion, rather than the total amount of MB in the effluent over that time.

TWA sampling of PACT: Handling, parametrics, interferents, and Limits of detection Desorption of MB from the SPME fibre over the time that lapsed between sample acquisition and analyses was evaluated. With respect to TWA sampling of the airstream in the PACT system, the fiber guide was buried into a septum (to seal the tip of the fibre guide), immediately following acquisition for a hold time of 0, 30, 60, or 195 min. Alternatively, the fibre guide was analyzed without being buried in a septum after hold times of 0 or 60
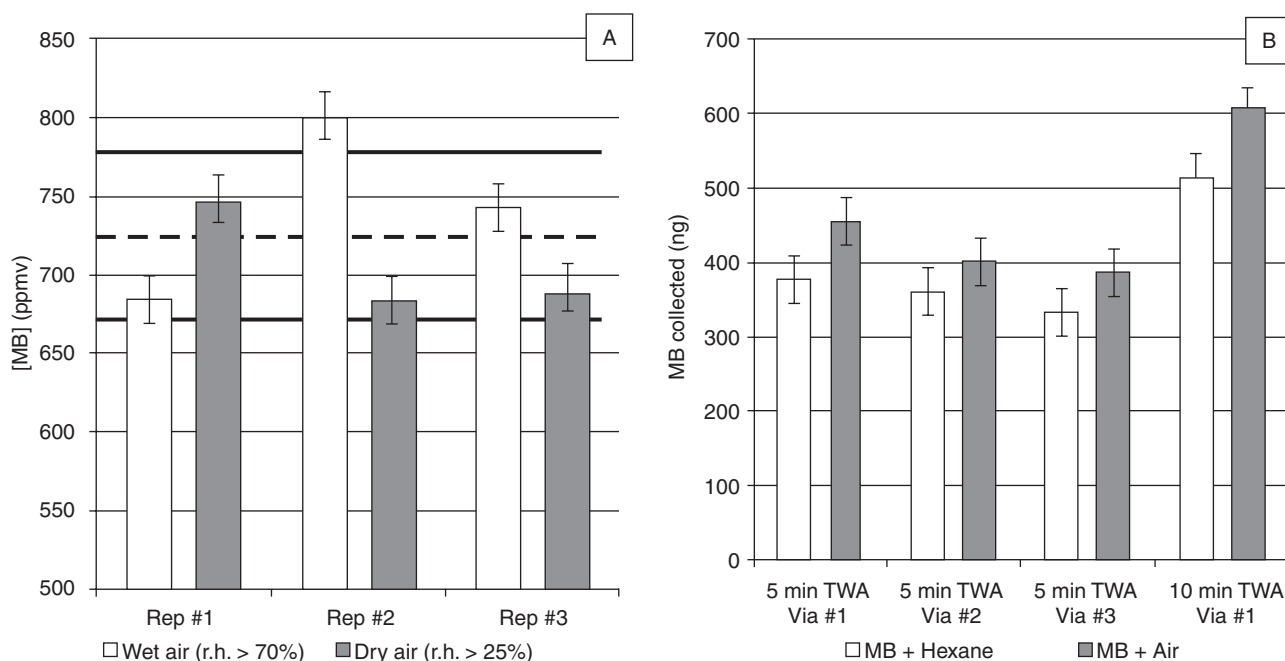
Fig. 2. The effects of interferents with values reported as $\bar{x} \pm s$: A, time-weighted average (TWA) sampling of methyl bromide concentrations ([MB]) from either humid ($\geq$70% r.h. or dry ($\leq$25% r.h.) airstreams (dashed horizontal line indicates the theoretical concentration, solid horizontal lines the 95% confidence intervals); B, TWA sampling of [MB] in static headspace with or without hexane

min. A linear least-squares analysis (Fig. 1) of the data (solid line = with septa: $R^2 = 0.2074$, $F_{1,46} = 12.0366$, $P = 0.0011$; dashed line = without septa: $R^2 = 0.8026$, $F_{1,26} = 105.707$, $P < 0.0001$) showed that burying the fibre into the septum resulted in minimal MB loss over –30 min (solid line), with just 0.089% loss per min. Without burying the fibre into a septum, a statistically significant loss (95% confidence interval) of MB occurred after –11 min (solid vertical line), consistent with a 0.4% loss of MB per min.

Experiments were conducted to address the possibility that a non-target compound, or interferent, could (compete for sorption sites on the fibre) and impact the quantification of MB using TWA sampling. The PACT system was metered to a [MB] of ca. 725 $\pm$ 53.13 ppmv ($\bar{x}$ $\pm$ 95% CI) with either –25% dry or –75% r.h. Wet airstreams and 6 channels ($n = 6$) were sampled for 15 min using the TWA approach. Three independent replicate analyses were performed for each condition and the [MB] was calculated from a calibration curve based on response under dry conditions. When mean [MB] for each of the six analyses was adjusted for model uncertainty, there was no significant difference between wet and dry conditions (Fig. 2A).

Hexane, which has a higher vapour pressure relative to H_2O (O'Neil, 2001) was selected as a surrogate volatile organic carbon (VOC) interferent

to MB quantification. A [MB] of ca. 1,040 ppmv was established in the static head space of 8 vials and then 1 mL aliquots of the head space were removed. Four of the vials received 1 mL aliquots of air, while the other four were fortified with 1 mL aliquots of –170,000 ppmv hexane in air. Three vials, both with and without hexane fortifications, were sampled with t = 5 min using the TWA technique, while the remaining two vials were with t = 10 min (Fig. 2B). Based on triplicate analyses, a consistently lower (357 $\pm$ 22 ng) ($\bar{x} \pm s$), but not statistically distinct, amount of MB was detected in the hexane-fortified vials relative to the control (416 $\pm$ 36 ng) with t = 5 min (T-test: t_{16} = –1.7304, $P < t = 0.0514$). Interference was more pronounced with t = 10 min, as ~ 20% less MB (510 $\pm$ 9 ng) ($n = 3$, $\bar{x} \pm s$) was detected in the hexane-fortified vial relative to the control (610 $\pm$ 14 ng MB) (T-test: t_4 = -10.337, $P > |t| = 0.0005$). This result indicates that with longer sampling times; compounds with physiochemical properties similar to hexane may affect TWA sampling of MB in the PACT system.

SPME is a sampling technique, not a method of analysis; the ability to resolve the signal for MB from any interferents and background depends on the method of analysis used. As with interference, the limit of detection (LOD) (Armbruster, 2008) is dependent on the instrument and parameters used for analysis. For TWA sampling of MB in the PACT

system, determining a LOD was complicated by physical limitations of the rotameters, which could not be metered below [MB] of ~1,100 ppmv. At this lower limit of [MB], the LOD was 14.7 ng MB based on 7 replicates ($n = 7$) TWA samplings with $t = 30$ s and subsequent GC-FID detection, which corresponds to an average "time-weighted" [MB] of 14.9 ppmv over the 30-min timespan ($t = 30$ min) when the ventilation of a postharvest chamber fumigation was simulated.

Application to ventilation effluent from chamber fumigations

Collectively, the results supported the use of TWA sampling for quantifying MB in the airstream of the PACT system. These results indicate similar utility when applied to the ventilation effluent from postharvest chamber fumigations, as the concentrations of MB and the sampling intervals will be the same as in this study. Future studies must examine how handling, parametrics, and interferents will affect the extension/application of TWA sampling for MB to commercial-scale fumigation chambers, commodity loads, and ventilation systems.

REFERENCES

Armbruster DA, Pry T (2008) Limit of blank, limit of detection and limit of quantitation. Clinical Biochemists Reviews **29**(Suppl 1), S49–52.

Bell CH, Price N, Chakrabarti B (1997) (In) The Methyl Bromide Issue. John Wiley & Sons, USA.

Hall WA, Bellamy DE, Walse SS (2015) Activated carbons from end-products of tree fruit and tree nut production as sorbents for removing methyl bromide in ventilation effluent from postharvest chamber fumigations. Journal of Agricultural and Food Chemistry **63**(12): 3,094–3,103.

Lary DJ (1996) Heterogeneous atmospheric bromine chemistry. Journal of Geophysical Research–Atmospheres **101**(D1): 1,489–1504.

Leesch JG, Knapp GF, Mackey BE (2000) Methyl bromide adsorption on activated carbon to control emissions from commodity fumigations. Journal of Stored Products Research **36**(1): 65–74.

Johnson JA, Walse SS, Gerik JS (2012) Status of alternatives for methyl bromide in the United States. Outlooks on Pest Management **23**: 53–58.

O'Neil, MJ. (2001) In: The Merck Index : An Encyclopedia of Chemicals, Drugs, and Biologicals. Whitehouse Station, Merck N.J. 2001.

Solomon S (1990) Progress towards a quantitative understanding of Antarctic ozone depletion. Nature, Landon **347**(6291), 347–354.

Yung YL, Pinto JP, Watson RT, Sander SP (1980) Atmospheric bromine and ozone perturbations in the lower stratosphere. Journal of Atmospheric Science **37**(2): 339–353.