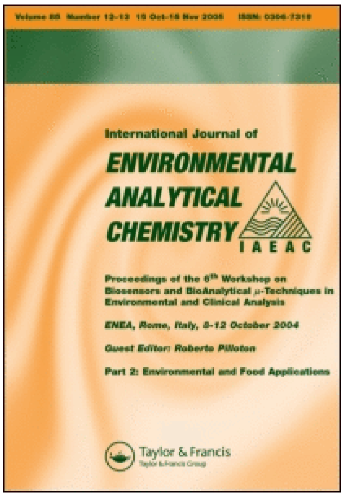

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A New Method for the Measurement of Airborne Formaldehyde Using Derivatization with 3,5-Bis(Trifluoromethyl) Phenylhydrazine and Analysis by GC-ECD and GC-MS/SIM

Adam M. Marsella[a]; James T. Purdham[a]; Scott A. Mabury[b]
[a] Gage Occupational and Environmental Health Unit, Department of Public Health Sciences, University of Toronto, Toronto, Ontario, Canada [b] Department of Chemistry, University of Toronto, Toronto, Ontario, Canada

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A NEW METHOD FOR THE MEASUREMENT OF AIRBORNE FORMALDEHYDE USING DERIVATIZATION WITH 3,5-BIS(TRIFLUOROMETHYL) PHENYLHYDRAZINE AND ANALYSIS BY GC-ECD AND GC-MS/SIM

ADAM M. MARSELLA[a], JAMES T. PURDHAM[a] and SCOTT A. MABURY[b*]

[a]Gage Occupational and Environmental Health Unit, Department of Public Health Sciences, University of Toronto, 223 College Street, Toronto, Ontario, Canada, M5T 1R4 and [b]Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada, M5S 3H6

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A new method was developed and described for the measurement of airborne formaldehyde using derivatization with 3,5-bis(trifluoromethyl)phenylhydrazine (TFMPH) coated onto silica solid phase extraction cartridges. Analysis by GC-ECD provides a detection limit of 74 ng formaldehyde per sample. A field study was conducted to compare the use of TFMPH to 2,4-dinitrophenylhydrazine (DNPH) and NIOSH method 3500 (chromotropic acid, CTA). Samples were collected from indoor and outdoor environments known or suspected to contain formaldehyde. Use of TFMPH with GC-ECD analysis correlates well with both methods (R^2=0.93, slope=1.07 vs. DNPH; R^2=0.99, slope=1.06 vs. CTA). Spiked samples were shown to be stable at least 7 days when stored at −20 °C. Analysis of samples by GC-MS with selected ion monitoring (GC-MS/SIM) also proved feasible. Laboratory and field results show the use of TFMPH to be viable for quantifying airborne formaldehyde in occupational and environmental samples.

Keywords: Formaldehyde; gas chromatography; derivatization; air sampling

INTRODUCTION

Aldehydes are significant constituents of indoor and outdoor air pollution, originating from a diverse range of sources including environmental tobacco smoke (ETS), out-gasing of building materials, the incomplete combustion of fossil

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* Corresponding author. Fax +1–416–978–3596. E-mail: Smabury@alchemy.chem.utoronto.ca

fuels and industrial processes such as smelting[1]. In general, there is widespread exposure to aldehydes in the home, environment and workplace. Aldehydes are important intermediates in the formation of photochemical smog[2]. While natural sources of aldehydes do exist through the photooxidation of naturally occurring hydrocarbons[3], exposure associated with human toxicity is almost exclusively linked to anthropogenic activities. Formaldehyde is the simplest aldehyde, but likely the most extensively studied due to its heavy use in industry[1] and highly toxic properties[4].

Examining the effects on human health of acute and chronic exposure to formaldehyde, as well as its role in tropospheric environmental chemistry, requires a reliable analytical technique for accurate quantification. In recent years, numerous attempts have been made at developing new methods for measuring airborne formaldehyde and other aldehydes through the reaction of aldehydes with a hydrazine, followed by detection of the resultant aldehyde-hydrazone derivatives[5–8]. One of the first hydrazines to gain widespread use in measuring airborne aldehydes was 2,4-dinitrophenylhydrazine (DNPH) coupled with analysis by high performance liquid chromatography with ultraviolet detection (HPLC-UV)[9]. Although this method is still extensively used[10–13], it suffers from several disadvantages. Because it is an HPLC technique, the resolution achievable is poor in comparison to gas chromatography (GC) methods. This lack of peak resolution can be problematic in complex air samples often encountered in the environment. Attempts have been made at analyzing DNPH hydrazones by GC[14]. This has not gained popular use, however, partially because of the relatively low volatility of DNPH and its hydrazones. Two additional disadvantages of using an HPLC technique include the large volumes of solvent waste produced and analysis times that are typically longer than those required with GC. Recently, Goelen *et al.*[15] conducted an inter-laboratory comparison utilizing several sampling and analysis techniques for formaldehyde, including DNPH. Their results indicated that, over the concentration range examined, approximately one third of the method-laboratory combinations using DNPH with HPLC-UV analysis were not able to comply with the minimum performance requirement of 30% overall uncertainty. This seems to point towards an opportunity at improving the state-of-the-art in formaldehyde sampling and analysis techniques.

In this paper, a new method is described for measuring airborne formaldehyde using silica solid phase extraction (SPE) cartridges impregnated with 3,5-bis(trifluoromethyl)phenylhydrazine (TFMPH) (Figure 1). Because of its six equivalent fluorine atoms, a TFMPH sample collection method opens the possibility of using ^{19}F-NMR in the analysis. The use of TFMPH with either electron capture detection (ECD) or mass spectrometry with selected ion monitoring (MS/SIM) offers several potential advantages over existing techniques, including increased sensitivity and selectivity. The two -CF_3 moieties in aldehyde-TFMPH derivatives should facilitate GC volatilization, possibly allowing for lower oven temperatures and shorter analysis times than similar existing methods. A preliminary attempt was made at quantifying the extent of these advantages in comparison to two existing techniques for measuring airborne formaldehyde: DNPH with analysis by HPLC-UV and NIOSH method 3500, chromotropic acid (CTA) with visible absorbance (VIS) analysis[16]. Finally, several aldehydes in addition to formaldehyde were analyzed as their TFMPH derivatives from spiked samples using GC-MS/SIM.

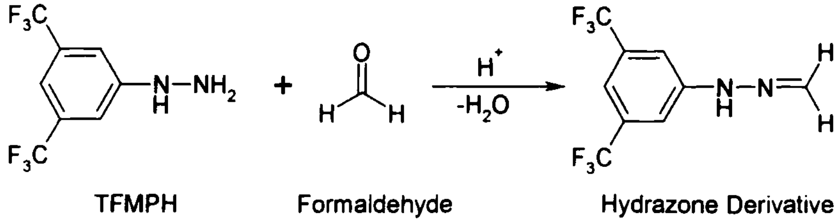

FIGURE 1 TFMPH structure and formaldehyde derivatization scheme

EXPERIMENTAL

Coating of silica SPE cartridges

All solvents were HPLC-grade (Caledon, Georgetown ON). The silica SPE cartridges used were of particle size 50–60 µm, with 500 mg sorbent per cartridge (Supelco, Oakville ON). Cartridges were washed with 5 mL acetonitrile and dried overnight in a desiccator. Following drying, 300 µL of a 10 mg/mL TFMPH solution (99% acetonitrile, 1% conc. H_3PO_4) was loaded onto each cartridge using a glass syringe fitted with a Teflon plunger. Batches of cartridges were subsequently dried for 24 hours under vacuum in a desiccator prior to sampling. To avoid possible aldehyde contamination of the sampling cartridges, a protocol similar to that employed by Grosjean and Grosjean[10] was employed. Several DNPH-coated filter papers were placed in the desiccator along with the cartridges. A DNPH-coated cartridge was placed on the inlet of the desiccator; these filters would act as passive samplers for any carbonyls present. In most cases, cartridges were used within 48 hours of being dosed with TFMPH. If longer storage times were required, the dry TFMPH cartridges were removed from the desiccator, capped with clean HDPE plastic caps, placed in a sealed plastic container which also contained several DNPH-coated filters and stored in the dark at 3–4 °C.

Generation of standards and evaluation of sampling flow rates

Standards were generated by spiking 100 µL of methanol containing known quantities of formaldehyde into a glass impinger apparatus (Figure 2). In this way, formaldehyde vapour was quantitatively loaded onto the TFMPH cartridges, mimicking their manner of introduction in actual field sampling. To ensure the reliability of this calibration technique, it was repeated using DNPH and the resultant standard curve compared to that obtained using an external hydrazone standard. The two calibration curves were not found to differ significantly, thereby providing an initial indication of the suitability of this vapour spiking technique for TFMPH calibration.

For TFMPH, sample collection flow rates of 250, 500, 750 and 1000 mL/min were evaluated (n=4) using the vapour spiking apparatus and a clean silica cartridge attached in series behind the TFMPH cartirdge. This was done to ensure that no TFMPH or hydrazone analyte was lost out the back of the cartridge during sample collection. The apparatus was spiked with 740 ng formaldehyde and allowed to run for 2 hours at each of the four flow rates. Both the primary TFMPH cartridges and the secondary breakthrough silica cartridges were analyzed by GC-ECD for the formaldehyde-TFMPH derivative and TFMPH.

To ensure that no formaldehyde was passing through the cartridges without being derivatized, a DNPH cartridge was attached in series behind a TFMPH cartridge, and 100 ug of formaldehyde gas introduced using the glass impinger apparatus. Nitrogen was passed through the system at 1000 mL/min for 2 hours, then the breakthrough DNPH cartridge analyzed for formaldehyde-DNPH hydrazone by HPLC-UV.

Cartridge elution

After sampling or vapour-spiking calibration, TFMPH-coated cartridges were slowly eluted with 3 mL of ethyl acetate at 2 mL/min. This was done by first eluting with 2 mL, centrifuging the cartridge to dryness and then eluting with an additional 1 mL of ethyl acetate and centrifuging a second time. This additional third millilitre of ethyl acetate was found to provide a slight increase in analyte recovery. Although acetonitrile did provide more complete cartridge elution in

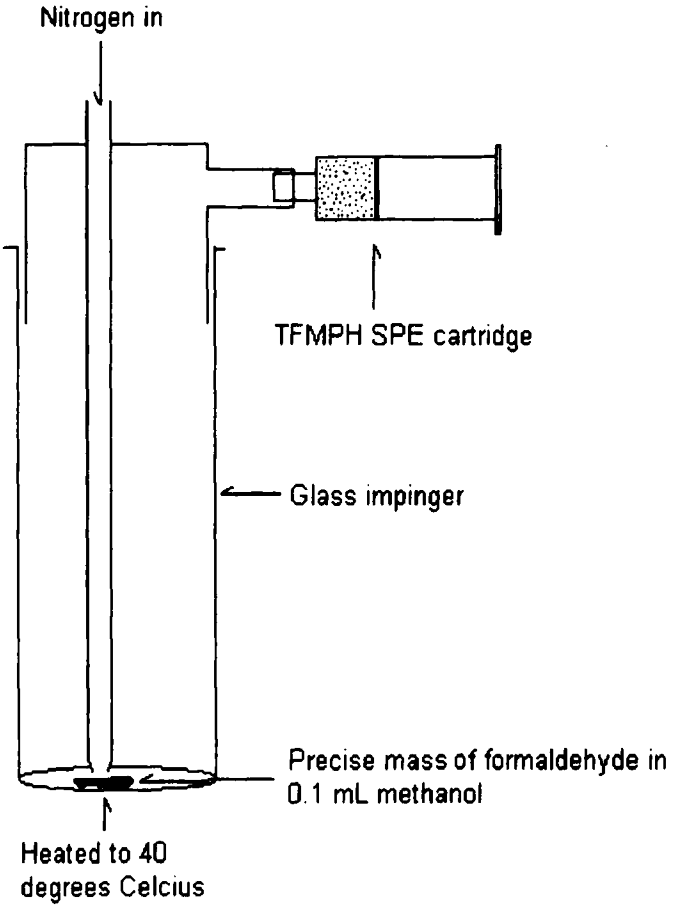

FIGURE 2 Vapour spiking apparatus used to spike TFMPH cartridges with known masses of formaldehyde

2 mL than ethyl acetate, we opted to use ethyl acetate to facilitate the possible use of GC with nitrogen phosphorous detection (NPD) in the future.

GC-ECD operating conditions

All GC-ECD analyses for the formaldehyde-TFMPH derivative were performed using a Perkin Elmer Autosystem XL GC fitted with a SPB-1701 column (0.32 mm × 30 m, 0.25 µm film thickness; Supelco). The injector and detector temperatures were 210 and 300 °C, respectively. The oven was temperature pro-

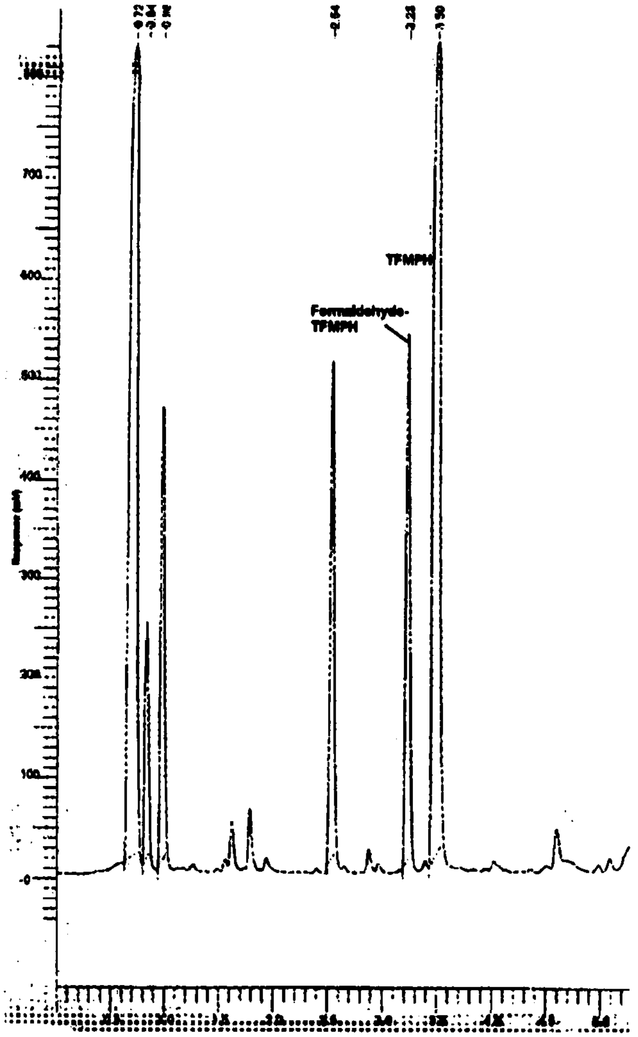

FIGURE 3 GC-ECD chromatogram showing TFMPH (3.5 min) and formaldehyde-TFMPH derivative (3.2 min)

grammed to begin at 105 °C for 2.0 minutes, ramp to 112 °C at 4 °C/min, holding for 0.2 minutes, then ramping to 230 °C at 45 °C/min and holding for 0.2 minutes. The ECD carrier gas was H_2 at 12 mL/min with a 3:1 split ratio. The make-up gas was N_2 at 30 mL/min. With these operating conditions, the formaldehyde-TFMPH hydrazone peak was observed at approximately 3.2 minutes (Figure 3).

Stability of the formaldehyde-TFMPH hydrazone

To establish proper sample storage protocols, an experiment was conducted to evaluate the stability of the formaldehyde-TFMPH analyte under various storage conditions. The treatments examined were (i) on the sampling cartridge at 3–4 °C in the dark, (ii) on the sampling cartridge at 20–25 °C in the dark, (iii) on the sampling cartridge at -20 °C in the dark and (iv) in 3 mL ethyl acetate at 3–4 °C in the dark, stored in sealed 5 mL amber sample vials. At T=0 days, cartridges were spiked with 50 μg of formaldehyde using the vapour spiking apparatus shown in Figure 2. Spiked cartridges were then divided equally among the 4 treatments. For treatment (iv), four cartridges were eluted immediately (serving as the T=0 day data point for all four treaments), analyzed and re-analyzed at each time point. Following T=0 days, two cartridges from treatments (i) to (iii) were eluted at each of the time-points depicted in Figure 4. All samples were analyzed by GC-ECD.

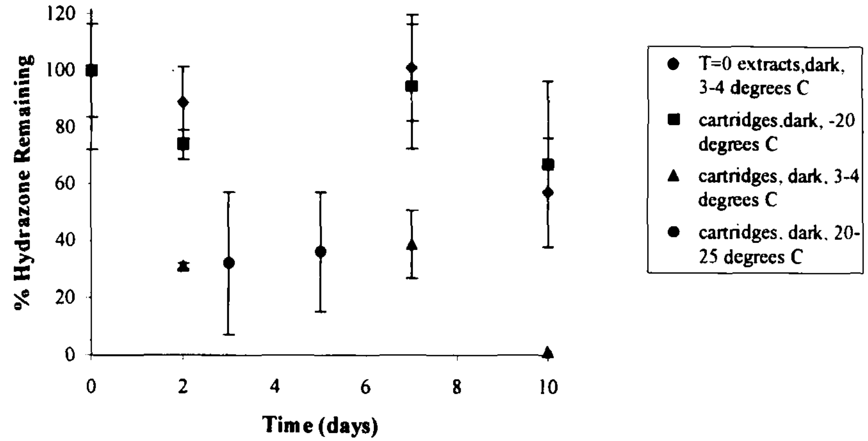

FIGURE 4 Results of formaldehyde-TFMPH stability experiment

Detection limit of the analytical method

While the overall method detection limit would be expected to vary with factors such as the sampling time, flow rates and final extraction volume, the detection limit of the analytical method was determined to be approximately 74 ng per sample by GC-ECD. This was determined by comparing two standard deviations from seven replicates of the blank and 74 ng per cartridge spiked samples, and can be regarded as a conservative estimate of the analytical detection limit. This detection limit was largely affected by residual formaldehyde-TFMPH in the blank samples. It was found that repeated recrystallization of the TFMPH from hot ethanol prior to dosing of the cartridges reduced this residual signal considerably, and would therefore also lower the analytical detection limit significantly.

Field comparison of TFMPH to DNPH and CTA

To validate the TFMPH method, samples were collected from a variety of occupational and environmental settings to reflect a range of aldehyde concentrations. When necessary, a sample volume correction was performed to account for samples collected at temperatures other than the calibration temperature of 25 °C. Side-by-side samples were collected using TFMPH cartridges, DNPH cartridges and, in some cases, NIOSH method 3500 (CTA)[16]. Sampling rates with TFMPH ranged from 60 to 150 mL/min. Higher flow rates were not used to avoid failure of the sampling pumps (Aircheck™ model 224-PCXR7; SKC, Eighty Four PA). Sampling times varied from 1 to 3 hours, depending on the formaldehyde concentrations anticipated. All TFMPH field samples were analyzed for the formaldehyde derivative by GC-ECD, with selected samples being re-analyzed by GC-MS/SIM to confirm peak identity. Any oxidative loss during sampling of formaldehyde-TFMPH via reaction with atmospheric oxidants other than ozone was accounted for using an "oxidation blank" run along side the collected samples. This oxidation blank consisted of a TFMPH cartridge attached behind a DNPH cartridge and KI ozone scrubber. The resultant decrease in hydrazone response relative to a blank cartridge was used as a correction factor for all environmental (<25 ppbv HCHO) samples collected on a given day of sampling.

The CTA method was not used in the majority of the environmental sampling, as this method is subject to numerous interferences from compounds expected to be encountered in ambient, environmental sampling[17–19]. For this reason, use of CTA was largely limited to occupational and indoor air quality settings. CTA was employed exactly as outlined in NIOSH method 3500[16]. Briefly, samples were collected in liquid glass impingers containing 20 mL of a 1% sodium bisulphite solution. Following sampling, aliquots from each sample were reacted with chromotropic acid and sulphuric acid and the resultant purple colour measured using a Perkin Elmer Model 55B spectrophotometer at 580 nm.

With DNPH, samples were collected at flow rates ranging from 80 to 900 mL/min. Following sampling, DNPH cartridges were capped with HDPE plastic caps and stored at 3–4 °C in the dark in a sealed plastic container containing several DNPH-coated filter papers. DNPH sample cartridges were slowly eluted with 2 mL acetonitrile at approximately 2 mL/min, then centrifuged to dry. Samples were analyzed using a Varian 9010 HPLC pump equipped with a Varian 9050 Variable Wavelength UV-VIS detector set at 360 nm. The mobile phase flow rate was 1 mL/min, ACN/water, gradient programmed as follows:

The column used was an Alltima™ C-18 end-capped column (25 cm × 4.6 mm, 5 µm particle size; Alltech)

Time (min)	0	2	10	15	16
% ACN	40	40	98	98	40

Applicability to other aldehydes

To show the potential for applying the use of TFMPH to other carbonyl compounds, a mixed standard of formaldehyde, acetaldehyde, acrolein, *n*-butyraldehyde and *p*-toluenaldehyde was prepared to deliver 100 µg of each aldehyde to a TFMPH cartridge using the vapour spiking apparatus shown in Figure 2. Analysis by GC-MS/SIM at *m/z* 228 was performed, and peak identities confirmed with an additional full-scan GC-MS run.

RESULTS AND DISCUSSION

A flow rate up to at least 1000 mL/min was found to be suitable for sample collection using the TFMPH cartridges. Even at 1000 mL/min, no formaldehyde, TFMPH or formaldehyde-TFMPH derivative loss was detected from the primary cartridge. For routine analysis, however, samples were not collected at flow rates greater than 150 mL/min to avoid pump failure. If lower detection limits are required, it is suggested that the cartridges used here be substituted with cartridges of a larger particle size (150–200 µm; Supelco, Oakville ON) to facilitate sample collection at higher flow rates.

The formaldehyde-TFMPH hydrazone was found to be stable at least 7 days as a stored extract at 3–4 °C and on the sampling cartridges at –20 °C. The results of the stability study are illustrated in Figure 4. Rapid degradation was observed, however, following storage of the sampling cartridges at room temperature or at 3–4 °C. The degradation was believed to be through the oxidation of the hydrazone derivative. This suspicion was partially confirmed with GC-MS (EI), which pointed to formation of the proposed oxidized product depicted in Figure 5(ii).

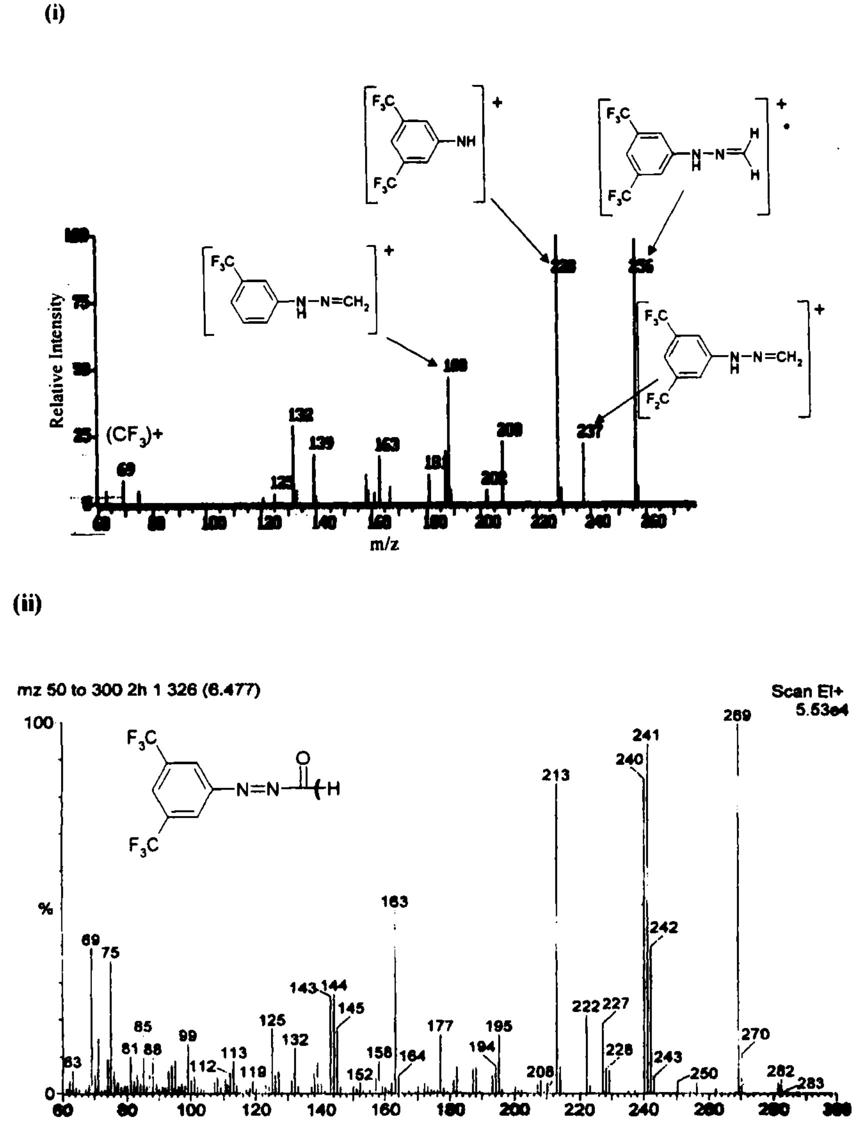

FIGURE 5 GC-MS (EI) fragmentation pattern of (i) formaldehyde-TFMPH derivative and (ii) suspected formaldehyde-TFMPH oxidation product following cartridge storage for 7 days

This rapid oxidative loss of the hydrazone derivative in the stability study necessitated two additional precautions during sampling at environmental concentrations of formaldehyde. First, commercially available potassium iodide ozone scrubbers (Supelco, Oakville ON) were attached in series to the front of each sampling cartridge. These scrubbers have been validated for the removal of the ozone interference observed with the use of DNPH at ozone concentrations ranging from 60 to 120 ppbv[20]. Given that formaldehyde-TFMPH appears to be more easily oxidized than the formaldehyde-DNPH derivative, this added precaution was taken with TFMPH when collecting outdoor samples of formaldehyde, since ozone would be expected to be present as a secondary pollutant outdoors. The efficacy of these KI scrubbers was examined on numerous occasions during outdoor sampling, and in each case provided a significant increase in formaldehyde-TFMPH recoveries relative to TFMPH samples collected without KI (Figure 6).

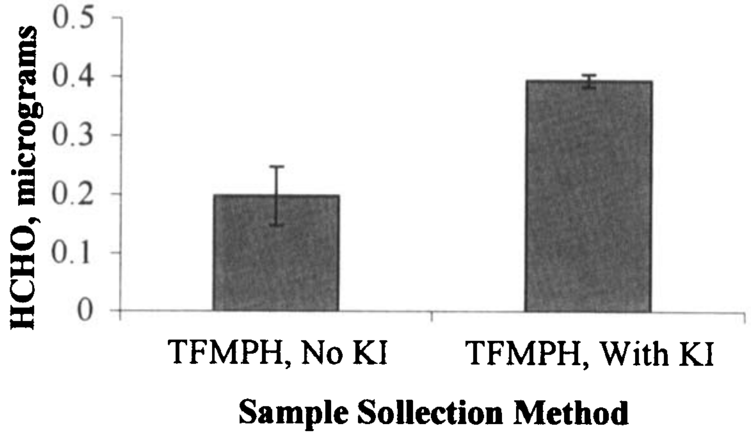

FIGURE 6 Effect of using in-line KI ozone scrubbers on measured airborne formaldehyde concentration using TFMPH method with GC-ECD analysis

The TFMPH method showed excellent agreement with both DNPH and CTA over the concentration range examined (Figure 7). Because formaldehyde-TFMPH to oxidant ratios would be higher in occupational settings, the oxidation blank correction factor was not required at higher (>25 ppbv) airborne formaldehyde concentrations to yield good agreement with DNPH and CTA. In comparing TFMPH to both existing methods, the slope was close to 1.0 (1.067 and 1.065 for DNPH and CTA comparisons, respectively). The y-intercept of 4 ppbv for CTA vs. TFMPH can be explained in part by the limited number of low concentration comparisons made between these two methods.

With a GC-ECD analytical detection limit of 74 ng/sample, the use of TFMPH is more sensitive than CTA at 500 ng/sample[17,21], but less sensitive than the

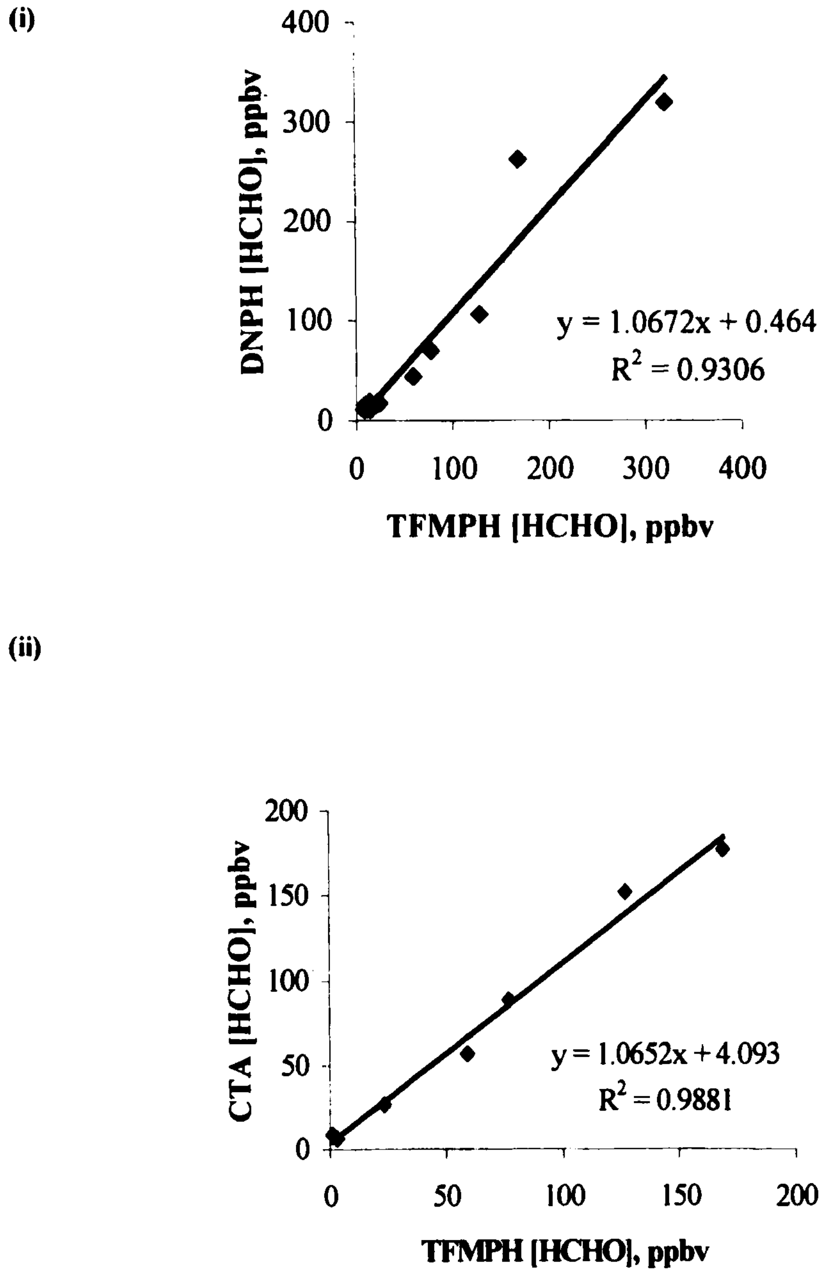

FIGURE 7 TFMPH versus (i) DNPH and (ii) CTA method comparison

value reported for DNPH of 9 ng/sample[11]. This detection limit can be improved to approximately 10 ng/sample through repeated recrystallization of the TFMPH to remove residual formaldehyde-TFMPH derivative, although a formal determination of this lower detection limit was not investigated. Lowering the detection limit would, overall, reduce the sampling time required to quantify low levels of formaldehyde. This was not an issue, however, for the concentrations and sampling times employed in collecting the samples presented here.

TABLE I Airborne concentration of HCHO measured using TFMPH, CTA and DNPH. *Environmental tobacco smoke (ETS) samples, taken from indoor environments during the consumption of tobacco products. **Ambient Environmental (AE) samples taken from downtown Toronto Location. na = not available

Sampling Location	*Date*	*[HCHO], ppbv*		
		TFMPH	*CTA*	*DNPH*
Embalming	Oct. 16/98	169	177	262
Embalming	Oct. 16/98	321	187	319
ETS*	Oct. 21/98	59	57	44
ETS	Oct. 21/98	77	89	70
ETS	Oct. 24/98	127	152	106
ETS	Oct. 24/98	23	27	18
AE	Mar. 17/99, 12–2 pm	13.7	na	18.7
AE**	Mar. 17/99, 2–4 pm	10.9	na	12.3
AE	Mar. 17/99, 4–6 pm	8.3	na	14.8
AE	Mar. 17/99, 6–8 pm	9.5	na	14
AE	May 20/99, 11 am-2 pm	10.4	na	11.7
AE	May 20/99, 2–5 pm	7.3	na	11.9
AE	May 20/99, 5–9 pm	14.2	na	11.2

Compared to previous studies of outdoor, ambient environmental levels of formaldehyde, the data collected here fall into the range of concentrations anticipated, although a direct comparison cannot be made due to spatial and temporal differences. Ambient HCHO concentrations from six Southern California locations measured by Grosjean[22] in 1988 and 1989 averaged 6.6 ppbv, with concentrations rising to as high as 29.4 ppbv. Similarly for Athens, Greece, an average HCHO concentration of 2.6 ppbv has been reported, with concentrations rising as high as 12.9 ppbv during eight sampling periods in 1995[23]. Ambient formaldehyde concentrations from two rural sites in Central Ontario averaged 1.6 and 1.8 ppbv in the summer of 1988[24]. The average outdoor HCHO concentration measured here from a site in downtown Toronto, taken as an average of all DNPH and TFMPH environmental samples presented in Table I, was 12.1 ppbv.

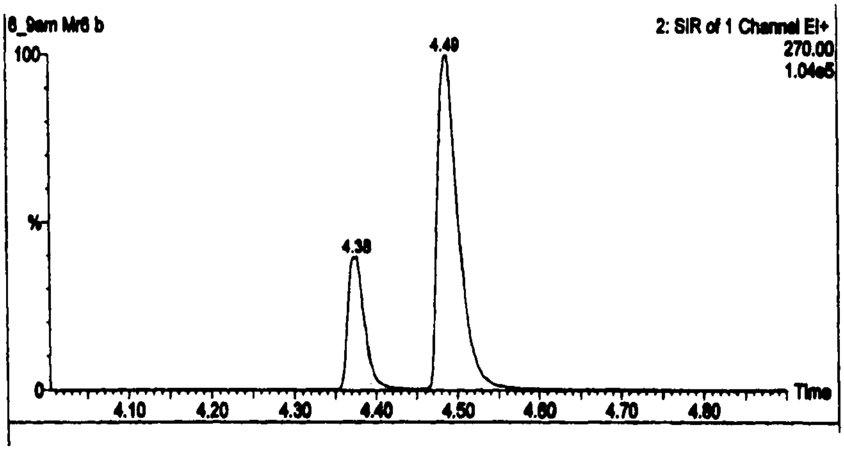

FIGURE 8 GC-MS/SIM chromatogram of *m/z* 270 showing baseline separation of both the *cis*- (4.38 min) and *trans*- (4.49 min) isomers of the acetaldehyde-TFMPH derivative. GC oven program identical to that used for GC-ECD, 70 eV ionization energy, ion source = 180 °C, SPB-1701 column (Supelco), 30 m × 0.32 m, 0.25 μm film thickness. Carrier gas H_2 at 14 psig, split flow at 25 mL/min

Analysis by GC-MS/SIM at *m/z* 270 for the acetaldehyde-TFMPH derivative also proved promising, yielding baseline separation of the *cis*- and *trans*-TFMPH derivative (Figure 8). Similarly, The combined five-aldehyde solution vapour spiked onto a TFMPH cartridge and analyzed by GC-MS/SIM at *m/z* 228 provides further evidence for the applicability of TFMPH derivatization to other carbonyls (Figure 9). The *cis*- and *trans*- isomers of acetaldehyde-TFMPH were not baseline resolved in this case, but collapsed into a single peak on the MDN-5 column. Also, the large peak observed for the acetone-TFMPH derivative in Figure 9 was attributed to glassware contamination, with the identity confirmed along with the other five derivatives using full-scan GC-MS. Some initial evidence has also been obtained by our laboratory for the applicability of using TFMPH in the derivatization of benzaldehyde and glutaraldehyde, with analysis by either GC-ECD or GC-MS/SIM.

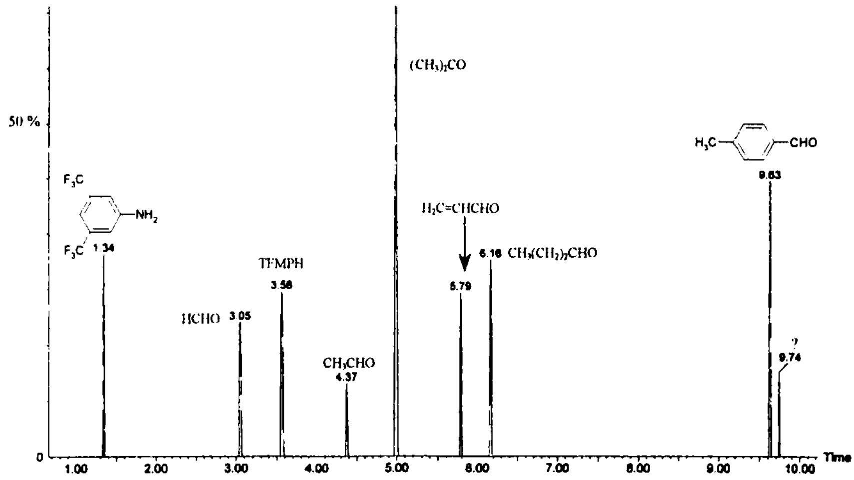

FIGURE 9 GC-MS/SIM chromatogram of *m/z* 228 for spiked sample extract. TFMPH derivatives of formaldehyde (3.05 min), acetaldehyde (4.37 min), acetone (4.99 min), acrolein (5.79 min), n-butyraldehyde (6.16 min), p-tolualdehyde (9.63 min) and an unknown peak (9.74 min). GC oven program T_1=105 °C, hold 2.0 min, 4 °C/min to T_2=112 °C, hold 0.2 min, 20 °C/min to T_3=230 °C, hold 2.0 min. Injector=210 °C. 70 eV ionization energy, ion source=180 °C. MDN-5 column (Supelco), 30 m × 0.25 mm, 0.25 μm film thickness. Carrier H_2 at 14 psig, split flow at 25 mL/min

CONCLUSIONS

From the comparative field data presented here, it can be concluded that TFMPH can effectively be used as a derivatizing agent in the quantification of airborne formaldehyde over the concentration range examined. The derivatizing agent is also potentially applicable to the measurement of other airborne aldehydes. Although susceptible to oxidation during the course of sample collection and storage, precautions can be taken to minimize this loss of analyte.

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References

1. National Research Council. *Formaldehyde and Other Aldehydes*. National Academy of Sciences: Washington, D.C., 1980.
2. J. Birks, "Oxidant Formation in the Troposphere", pp. 233–256 in *Perspectives* in *Environmental Chemistry*, D.L. Macalady Ed., Oxford University Press, New York, 1998.
3. P. Carlier, H. Hannachi and G. Mouvier, *Atmos. Environ.*, **20**, 2079–2099 (1986).
4. B. Hileman, *Environ. Sci. Technol.*, **18**, 216–225 (1984).
5. D.W. Lehmpuhl and J.W. Birks, *J. Chromatog. A*, **740**, 71–81 (1996).
6. W. Schmied, M. Przewosnik and K. Bachmann, *Frezenius' Z. Anal. Chem.*, **335**, 464–472 (1989).
7. A. Buldt and U. Karst, *Anal. Chem.*, **69**, 3617–3622 (1997).
8. A. Buldt and U. Karst, *Anal. Chem.*, **71**, 1893–1898 (1999).
9. K. Kuwata, M. Uebori, H. Yamasaki, Y. Kuge and Y. Kiso, *Anal. Chem.*, **55**, 2013–2016 (1983).
10. E. Grosjean and D. Grosjean, *Intern. J. Environ. Anal. Chem.*, **61**, 343–360 (1995).
11. D. Grosjean, *Environ. Sci. Technol.*, **25**, 710–715 (1991).
12. E. Koivusalmi, E. Haatainen and A. Root, *Anal. Chem.*, **71**, 86–91 (1999).
13. P. Kalabokas, J. Hatzianestis, J. Bartzis and N. Mimikos, *Fresenius Environ. Bull.*, **32**, 124–130 (1997).
14. I. Degraff, L. Nolan and A. Fiorante, *The Reporter* (Supelco), **15**, 3 (1996).
15. E. Goelen, M. Lambrechts and F. Geyskens, *Analyst*, **122**, 411–419 (1997).
16. National Institute for Occupational Safety and Health. *NIOSH Manual of Analytical Methods*, Fourth Edition, *Formaldehyde by VIS*; method 3500, 1994.
17. National Institute for Occupational Safety and Health. NIOSH Method No. S327 Failure Report, NIOSH/OSHA Standards Completion Program Contract Report, Cincinnati OH, 1976.
18. R.R. Miksch, D.W. Anthon, L.Z. Fanning, C.D. Hollowell, K. Revzan and J.G. Glanville, *Anal. Chem.*, **53**, 2118–2123 (1981).
19. National Institute for Occupational Safety and Health. *NIOSH Manual of Analytical Methods*, Second Edition, V.1, P&CAM 125, NIOSH Publ. 77-157-A, 1977.
20. T.E. Kleindienst, E.W. Corse, F.T. Blanchard and W.A. Lonneman, *Environ. Sci. Technol.*, **32**, 124–130 (1998).
21. User check, Southern Research Institute, NIOSH Sequence #3500 (Unpublished, November 10, 1983).
22. D. Grosjean, *Environ. Sci. Technol.*, **25**, 710–715 (1991).
23. P. Kalabokas, J. Hatzianestis, J. Bartzis and N. Mimikos, *Fresenius Environ. Bull.*, **6**, 172–177 (1997).
24. P.B. Shepson, D.R. Hastie, H.I. Schiff, M. Polizzi, J.W. Bottenheim, K. Anlauf, G.I. Mackay and D.R. Karecki, *Atmospheric Environ.*, **25A**, 2001–2015 (1991).