# A NEW METHOD FOR THE MEASUREMENT OF AIRBORNE FORMALDEHYDE USING DERIVATIZATION WITH 3,5-BIS(TRIFLUOROMETHYL)PHENYLHYDRAZINE

by

Adam Manuele Marsella

A Thesis submitted in conformity with the requirements
for the degree of Master of Science
Graduate Department of Community Health
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Abstract

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Chairperson of the Supervisory Committee: Professor James T. Purdham
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A new method is described and validated for the measurement of airborne formaldehyde using solid phase extraction (SPE) cartridges impregnated with 3,5-bis(trifluoromethyl)phenylhydrazine (TFMPH). Analysis by gas chromatography with electron capture detection (GC-ECD) provides a detection limit of 74 ng formaldehyde per sample. A field study was conducted to compare the use of this method to the US Environmental Protection Agency (EPA) method TO-11, which uses 2,4-dinitrophenylhydrazine (DNPH) and the National Institute for Occupational Safety & Health (NIOSH) chromotropic acid (CTA) method (NIOSH method 3500). Samples were collected from a variety of 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=1.09 vs. DNPH; $R^2$=0.96, slope=1.01 vs. CTA). Spiked samples were shown to be stable at least 14 days when stored at -20 °C. Analysis of samples by

gas chromatography-mass spectrometry with selected ion monitoring (GC-MS/SIM) has also proved feasible, with a detection limit comparable to that obtained by GC-ECD. All instrument calibrations were carried out by vapour spiking precise masses of aldehyde onto the sampling cartridges. For field sampling at environmental concentrations (<25 ppbv) of formaldehyde, oxidation of the formaldehyde-TFMPH hydrazone can be corrected for through the use of potassium iodide ozone scrubbers and by performing an 'oxidation blank' subtraction from the standard curve. Laboratory and field results show the use of TFMPH to be viable for quantifying airborne formaldehyde in occupational and environmental samples. Also demonstrated is the potential for applying TFMPH as a derivatizing agent for measuring other airborne carbonyls.

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*"And lots of times, moreover, we have the impression not only of being blind, but of being blind elephants at a watch-mender's desk, because our fingers are too crude to handle those tiny things that we have to attach or detach."*

-Primo Levi

# GLOSSARY

**TFMPH.** 3,5-bis(trifluoromethyl)phenylhydrazine.

**DNPH.** 2,4-dinitrophenylhydrazine.

**CTA.** Chromotropic acid.

**GC-ECD.** Gas chromatography with electron capture detection.

**GC-NPD.** Gas chromatography with nitrogen-phosphorous detection.

**HPLC-UV.** High performance liquid chromatography with ultraviolet detection.

**Formaldehyde.** A ubiquitous airborne pollutant and suspected human carcinogen. The simplest of the aldehydes.

**SPE.** Solid phase extraction.

**GC-MS (EI).** Gas chromatography with mass spectrometric detection using an electron impact ion source.

**GC-MS (SIM).** Gas chromatography with mass spectrometric detection using an electron impact ion source with selected ion monitoring.

**$^{19}$F-NMR.** Fluorine nuclear magnetic resonance.

*Chapter 1*

# 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 fuels and industrial processes such as smelting (National Research Council, 1980). In general, there is ubiquitous exposure to aldehydes in the home, environment and workplace. While natural sources of aldehydes do exist through the photooxidation of naturally occurring hydrocarbons (Carlier, 1986), exposure associated with human toxicity is almost exclusively linked to anthropogenic activities.

## 1.1. Toxicity of Formaldehyde

Formaldehyde is the simplest aldehyde, but likely the most extensively studied due to its widespread use in industry (National Research Council, 1980) and because of its highly toxic properties (Hileman, 1984). More specifically, workplace studies of workers exposed to formaldehyde as well as controlled exposure studies have shown the target organs to be the skin, eyes and respiratory tract (Sim and Pattle, 1957; Schuck et al., 1966; Roth, 1969; Porter, 1975). Death following acute poisoning with inhaled formaldehyde has been reported (Porter, 1975), but is rare.

Fairly low-level (0.01-2.0 ppmv) occupational exposures to formaldehyde have been reported to cause asthma, mucous membrane irritation, neurophsychological effects and malignant disease (Ritchie and Lehen, 1987; Thrasher *et al.*, 1987; Horvath *et al.*, 1988). Although asthmatic attacks caused by formaldehyde can in some cases be the result of

formaldehyde sensitization, formaldehyde appears to more commonly act as a direct irritant to the upper airways of persons who already suffer from asthma from other causes (National Research Council, 1980). Although asthmatic symptoms are only evident in some sensitized subjects, formaldehyde does produce bronchioconstriction at irritant concentrations in most individuals (National Research Council, 1980).

Acute inhalation of formaldehyde causing sensory irritation has been shown to be concentration dependent (ACGIH formaldehyde documentation, 1991). In addition to being a severe lachrymator, formaldehyde is also known to cause irritation of the nose, throat and lungs. Cellular changes in the upper respiratory tract have also been observed in animals exposed to formaldehyde (ACGIH formaldehyde documentation, 1991). After exposing rats to 0.5 ppmv formaldehyde for three days, mucociliary action in the nasal cavity was inhibited (Edling *et al.*, 1985). It is believed that this inhibition of mucociliary activity can hinder the draining of secretions from the sinuses and the lacrimal glands, one of the normal functions of the nasal cavity (USEPA, 1987).

Biochemically, aliphatic aldehydes such as formaldehyde are direct-acting bioreactive electrophiles (Schultz *et al.*, 1994). Because they require no metabolic activation to exert their toxicities, aliphatic aldehydes are more toxic at lower concentrations than unreactive compounds of equal hydrophobicity (Schultz *et al.*, 1994). Reaction is most likely to occur with nucleophilic groups in proteins and nucleic acids. Interaction with these nucleophiles is through addition at the carbonyl group of the aldehyde (Hermens, 1990). The high degree of aliphatic aldehyde acute toxicity at or near the site of exposure (eyes, skin and upper respiratory tract) can therefore be explained by the highly reactive nature of these compounds in their parent forms.

Numerous agencies including the International Agency for Research on Cancer (IARC) classify formaldehyde as a probable human carcinogen (IARC, 1982). This is due in part to the induction of squamous cell carcinomas and numerous benign tumors in the nasal passages of mice and rats exposed to formaldehyde (Feinman, 1988). This animal data is

further supported by human case studies involving prolonged occupational exposure to formaldehyde (Hernberg *et al.*, 1983; Blair *et al.*, 1986; Vaughn *et al.*, 1986a; Vaughn *et al.*, 1986b).

## 1.2. Analytical Methods for Formaldehyde

Establishing standards and estimating risk associated with exposure to formaldehyde requires a good analytical technique for accurately quantifying the exposure. Numerous techniques have been proposed, with varying degrees of success. Some noteworthy examples include the following:

### 1.2.1. Colourimetric Methods

The most frequently used and accepted of these methods is NIOSH method 3500 (1994), *Formaldehyde by Visible Absorbance (VIS)*. Air samples are passed through liquid impingers containing a 1% sodium bisulphite solution. For colour development, chromotropic acid and sulphuric acid are added prior to measuring absorbance at 580 nm. An explanation of the underlying theory behind the development of the resulting purple colour is provided by Fiegel (1966).

Although this chromotropic acid (CTA) method is highly sensitive with an estimated limit of detection (LOD) of 0.5 µg per sample (NIOSH/OSHA Standards Completion Program Contract Report, 1976; Southern Research Institute, 1983), numerous interferences have been reported. Interfering compounds include oxidizable organic materials (NIOSH/OSHA Standards Completion Program Contract Report, 1976), phenol (Miksch, 1981), ethanol and higher molecular weight alcohols, olefins, aromatic hydrocarbons (Sleva, 1965) and cyclohexane (NIOSH Manual of Analytical Methods, 1977). The most significant of these is the interference from phenol, which may produce a 15% negative bias at phenol to formaldehyde ratios as low as 0.3 (Miksch,

1981). These interferences make the CTA method ill-suited for trace environmental sampling, where phenol and other interfering compounds are often present at significant concentrations relative to formaldehyde. Also limited is the applicability of NIOSH method 3500 to occupational hygiene sampling. This is due to interfering compounds often used in conjunction with formaldehyde in industrial settings, and because of the awkwardness of using glass impingers containing a liquid collection medium for personal sampling.

Another common colourimetric method for measuring airborne formaldehyde utilizes pararosaniline as the chromagen. However, unlike the CTA method, this method is prone to significant interferences from other aldehydes, including acetaldehyde and acrolein (Miksch *et al.*, 1981). In addition, the CTA method was found to have a greater overall accuracy and collection efficiency than the pararosaniline method, likely due to the increased sample stability afforded by the 1% sodium bisulphite absorbing solution (Petreas *et al.*, 1986).

### 1.2.2. Polarographic Methods

An example of a polarographic method for formaldehyde is provided by Septon and Ku (1982). Using this method, air samples are collected in midget fritted glass bubblers containing a 10% methanol aqueous solution. Methanol is included to prevent polymerization of the formaldehyde. Following sampling, the collected formaldehyde is derivatized with 2,4-dinitrophenylhydrazine (DNPH) and the resulting hydrazone derivative measured by differential pulse polarography in acetate buffer at a dropping mercury electrode. As with the CTA method described above, this method suffers from an inconvenient sampling apparatus for application to personal sampling. Overall, polarographic techniques have not been widely applied to measuring airborne aldehydes and most existing methods have been poorly documented, making an assessment of polarographic techniques for formaldehyde difficult and incomplete (Otson and Fellin, 1988).

### 1.2.3. High Performance Liquid Chromatography (HPLC) Methods

The most widely used and accepted of HPLC methods is derivatization of airborne formaldehyde on silica or C-18 solid phase extraction (SPE) cartridges impregnated with DNPH, followed by analysis of the resultant hydrazone by HPLC-UV at 360-370 nm (Kuwata *et al.*, 1983). In addition to formaldehyde, this derivatization technique is routinely applied to measure numerous other aldehydes including acrolein, acetaldehyde and glutaraldehyde (Goelen *et al.*, 1997). The chemical structure of DNPH and a general schematic of the derivatization is provided in figure 1.1. Acidic conditions are used to facilitate the acid-catalyzed dehydration reaction which forms the aldehyde-DNPH hydrazone analyte. DNPH solid phase derivatization remains a popular technique due to its ease of use and adequate sensitivity for occupational and environmental levels of aldehydes.

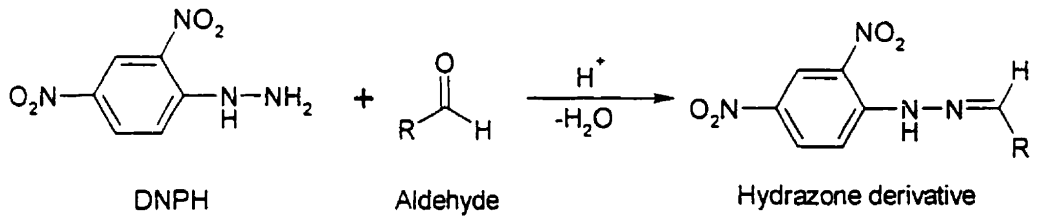


Figure 1.1: DNPH structure and aldehyde derivatization scheme.

While widely accepted and validated (Druzik *et al.*, 1990; Grosjean and Grosjean, 1995; Kleindienst *et al.*, 1998), the use of this method has several disadvantages. Most notably, because the separation technique is HPLC, the chromatographic resolution is not as great as the peak resolution achievable with a gas chromatographic (GC) method. This limits the accuracy of the DNPH HPLC-UV method when analyzing aldehydes in complex air samples. Also, unlike GC methods, HPLC methods produce significant amounts of solvent waste. In terms of analyte detection, HPLC with UV

detection does not offer as much sensitivity as many of the GC detectors currently available.

An additional problem may arise when sampling in the presence of ozone. It has been well documented that the DNPH reagent can react with ozone to form several products (Arnts and Tejada, 1989; Smith *et al.*, 1989). These reaction products can co-elute with the hydrazone(s) of interest, making necessary the use of dual wavelength detection to confirm or refute the presence of interferences (Pötter and Karst, 1996). This ozone interference can be overcome with the use of potassium iodide scrubbers to remove the ozone before the air sample reaches the DNPH cartridge. However, these ozone scrubbers require moderate water concentrations (>4000 ppmv; RH > 10% at 25 °C) to be effective (Kleindienst *et al.*, 1998). A recent attempt has been made, with some success, at utilizing 1-methyl-1-(2,4-dinitrophenyl)hydrazine instead of DNPH as the derivatizing agent for HPLC-UV analysis, in the hope that this agent would have a more predictable reactivity towards ozone (Büldt and Karst, 1997).

Goelen *et al.* (1997) observed that not all aldehyde-DNPH hydrazone derivatives are stable on the SPE cartridges. With the sampling time ranging from 1 to 2.5 hours and a relative humidity of 42 to 80%, fewer than 80% of the laboratories participating in this study were able to achieve an overall uncertainty less than 30% for formaldehyde when the concentrations were varied from 0.312 to 1.46 ppmv. Nevertheless, derivatization with DNPH followed by HPLC-UV analysis remains among the most common techniques used for measuring airborne aldehydes. This can be attributed to the fact that the method is relatively easy to use and is well validated with respect to parameters such as sample collection efficiencies, potential interferences and analysis protocols. Also, the use of DNPH with HPLC-UV does provide results within 30% of the true value in the majority of cases (Goelen *et al.*, 1997).

Another important derivatizing agent used in HPLC analysis of airborne carbonyls is dansylhydrazine (DNSH). This compound forms fluorescent hydrazones with carbonyls, allowing for the use of highly sensitive fluorescence detection (Schmied *et al.*, 1989; Nondek *et al.*, 1992). The detection limits of this method for formaldehyde and acetaldehyde are quite low: 0.1 ppbv for a 1 litre air sample collected at 100 ml/min (Nondek *et al.*, 1992). Figure 1.2 gives the chemical structure of DNSH and the carbonyl derivatization scheme.

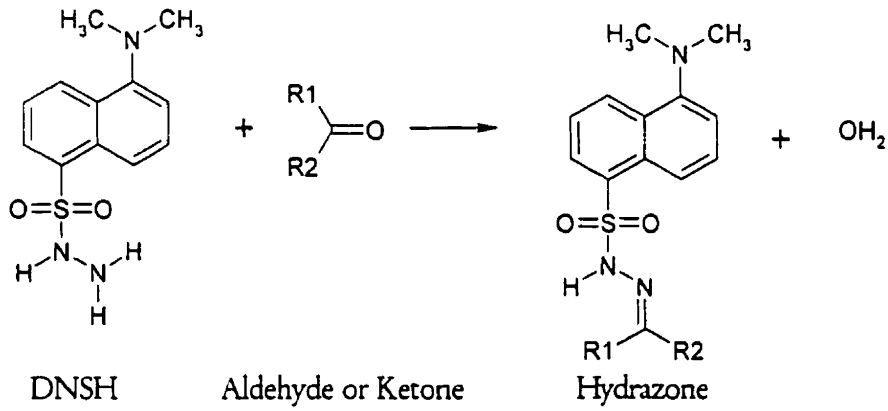


Figure 1.2: DNSH structure and aldehyde derivatization scheme.

## 1.2.4. Direct GC Methods

Several direct GC methods have been described in the literature. These techniques make use of a formaldehyde adsorbent often comprised of molecular sieve 13X. One such method, employed by Yokouchi *et al.* (1979), made use of the molecular sieve 13X to sample formaldehyde. Following sampling, the formaldehyde was thermally desorbed onto the analytical column and detected by mass spectrometry (MS) using mass fragments (*m/z*) 29 and 30. Unfortunately, storage studies showed the formaldehyde to be stable on the sieve for only 24 hours at ambient temperatures, even when the adsorption tube was sealed with silicone rubber. While this technique was

found to be quite sensitive for formaldehyde (0.3 ppb detection limit for a 1 L sample with a signal-to-noise ratio of 3 or more), direct GC methods in general have not found widespread application due in part to the poor stability of the aldehyde analytes and the GC detector limitations inherent in analyzing underivatized aldehydes (Otson and Fellin, 1988).

### 1.2.5. GC Derivatization Methods

In recent years, derivatization techniques for measuring airborne aldehydes by GC have gained considerable attention as possible alternatives to the use of DNPH with HPLC-UV analysis. Indeed, some have gone as far as attempting to analyze aldehyde-DNPH hydrazone derivatives by GC, usually with flame ionization detection (FID) (DeGraff *et al.*, 1996). Since most methods utilizing DNPH on either C-18 or silica SPE cartridges call for elution with acetonitrile, use of a nitrogen phosphorous detector (NPD) for the aldehyde-DNPH hydrazones would require selection of another eluting solvent, since acetonitrile would overload the detector. Regardless, DNPH is by no means the optimum derivatizing agent for the analysis of aldehydes by GC, since its two nitro-moieties greatly inhibit the molecule's volatility, the key limiting factor.

Most work has gone towards developing new derivatizing agents better suited for analysis by GC. One widely accepted technique is NIOSH method 2541, *Formaldehyde by GC* (1994). This method calls for the derivatization of airborne formaldehyde on XAD-2 solid sorbent tubes impregnated with 2-(hydroxymethyl)piperidine (HMP). Once sampling is complete, the oxazolidine derivative of formaldehyde is analyzed by GC-FID. Although the sampling device is more convenient and suffers from fewer interferences than NIOSH method 3500, this method is not as sensitive as the CTA method and is therefore only useful in occupational environments; the estimated LOD of method 2541 is 1 μg per sample, compared to 0.5 μg per sample for method 3500 (NIOSH Manual of Analytical Methods, Fourth Edition, 1994).

Lempuhl and Birks (1996) developed the use of 2,4,6-trichlorophenylhydrazine (TCPH) for the derivatization of airborne formaldehyde with subsequent analysis by GC with electron capture detection (ECD). Unlike the use of DNPH in GC analysis, TCPH has the added advantage of being sufficiently volatile for easier GC analysis without the problem of thermal decomposition associated with DNPH (Hoshika and Takata, 1976). Unlike most DNPH methods described in the literature, the TCPH method requires no acid addition to the sampling device to aid in the formation of the analyte hydrazones. Instead, a sampling device incubation time of 6 min at 100 °C following sampling was found to be sufficient in achieving a 100% reaction between carbonyls and the TCPH. Acid was not used to avoid the acid-catalyzed decomposition of the sampling device stationary phase, an outcome which could potentially reduce the life of the sampler (Lempuhl and Birks, 1996).

Another hydrazine derivatizing agent used for aldehydes and well suited to GC-ECD analysis is pentafluorophenylhydrazine (Hoshika and Muto, 1978), which has more recently been applied to assaying malondialdehyde in biological samples with GC-MS analysis (Yeo *et al.*, 1994). Derivatization with 2-hydrazinobenzothiazole followed by GC-NPD analysis has been applied to volatile aldehydes formed during lipid peroxidation (Stashenko et al., 1996).

Also used as a reagent for formaldehyde derivatization is O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA). This reagent, in a manner similar to the hydrazines described above, reacts with carbonyl compounds to form the corresponding oxime derivatives. It has been applied to a variety of carbonyls in aqueous solutions (Glaze *et al.*, 1989) and recently in a passive sampler for OSHA regulated aldehydes (Tsai and Que Hee, 1999). Analysis of oxime derivatives using this reagent has been performed by GC-ECD, GC-MS (EI), GC-MS (SIM) and HPLC-MS (Glaze *et al.*, 1989; Le Lacheur *et al.*, 1993; Tsai and Que Hee, 1999).

A summary of the detection limits and sampling parameters for some of the noteworthy methods described above is given in Table 1.1.

## 1.3. Analysis of Environmental Samples with Hydrazine Derivatization: Some Special Considerations

Several added considerations must be made when sampling at low (<50 ppbv), environmental concentrations of formaldehyde. As mentioned above, DNPH and its corresponding hydrazone derivatives are susceptible to oxidation by ozone (Smith, 1983; Smith et al., 1989; Arnts and Tejada, 1989). Kleindienst *et al* (1998) found that an ozone concentration of 120 ppbv produced, on average, a 54% negative bias when using DNPH and sampling on silica gel SPE cartridges at relative humidities representative of ambient conditions. This finding was reversed on C-18 SPE's, where the same relative humidities produced an average of a 23% *positive* bias at 120 ppbv ozone. No explanation of this observation was provided, and the identity of the multiple oxidized products was not confirmed. Various systems have been proposed for dealing with this interference, such as the use of potassium iodide denuders or scrubbers to remove the ozone as reported and validated by Kleindienst *et al.* (1998). Also relevant is the use of sodium thiosulfate as an ozone scavenger, although this method of ozone removal would likely only be applicable to sampling protocols that do not require strong acidic conditions, such as the TCPH or DNSH methods described above (Lempuhl and Birks, 1996).

Although the magnitude and nature of the ozone interference has been investigated for DNPH, no such evaluation exists for the majority of the other hydrazine derivatization methods. This is largely because of their limited use in comparison to the more popular DNPH. Since all hydrazines would be expected, to a lesser or greater extent, to be susceptible to this oxidation, any significant oxidative interferences during sampling must be accounted for.

## 1.4. Study Rationale and Objectives

The overall objective of this work was to develop a new indirect GC derivatization method for measuring airborne concentrations of formaldehyde. The use of 3,5-bis(trifluoromethyl)phenylhydrazine (TFMPH) (Figure 1.3) as a derivatizing agent for formaldehyde followed by GC with ECD offers several potential advantages over existing

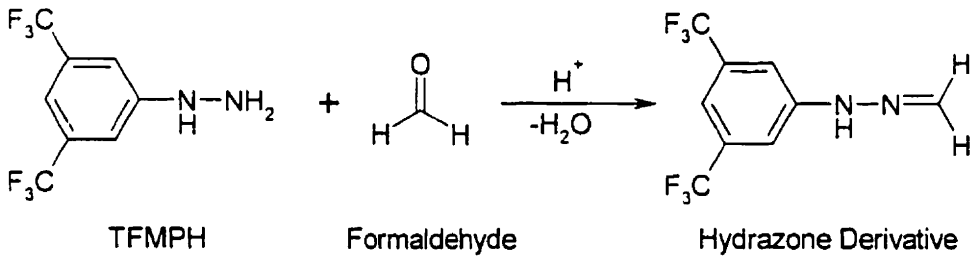


Figure 1.3: TFMPH structure and aldehyde derivatization scheme.

methods, including increased sensitivity and selectivity. The sampling device (Figure 1.4) offers a high degree of field portability and convenience. Through the course of developing this new method, an attempt to quantify the extent of these advantages was made against a widely used and accepted method: the use of DNPH as a derivatizing agent impregnated onto C-18 and silica SPE cartridges, followed by HPLC-UV analysis (Kuwata *et al.*, 1983). Use of DNPH has been extensively documented with respect to such parameters as derivative stability, method detection limit, reproducibility, precision and accuracy (Druzik *et al.*, 1990; Grosjean & Grosjean, 1995; Goelen *et al.*, 1997; Gilpin *et al.*, 1997; Kleindienst *et al.*, 1998). It has also been endorsed by the USEPA for measuring airborne formaldehyde levels in the environment (USEPA method TO11A). Also compared was the use of TFMPH and

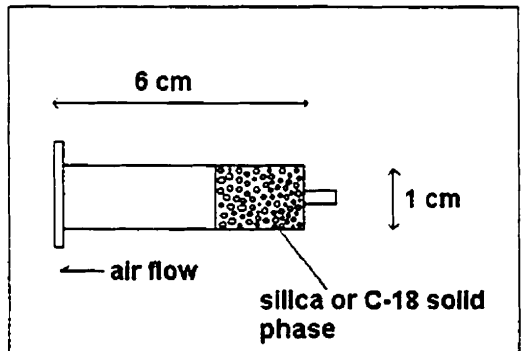


Figure 1.4: TFMPH sampling device.

NIOSH method 3500 (1994), the CTA colourimetric method. Comparisons were made using a variety of environmental and occupational settings.

| | METHOD | | | | |
|---|---|---|---|---|---|
| | Chromotropic Acid | HMP | DNPH | TCPH | DNSH |
| References: | NIOSH method 3500 | NIOSH method 2541 | (1) Grosjean, 1991<br>(2) Zhang *et al.*, 1994 | Lehmpuhl & Birks, 1996 | Nondek *et al.*, 1992 |
| Analysis: | UV-VIS | GC-FID | HPLC-UV | GC-ECD | HPLC-fluorescence |
| Method Detection Limit: | 0.5 ug/sample (0.28 ppbv if sampling @ 1000 mL/min for 24 h) | 1 ug/sample (5.7 ppbv if sampling @ 100 mL/min for 24 h) | (1) 9 ng /cartridge (0.02 ppbv if sampling @ 250 mL/min for 24 h)<br>(2) 0.1-0.4 ppbv | 0.1 ppbv | 0.1 ppbv |
| Flow Rate: (mL/min) | 200-1000 mL/min | 10-100 mL/min | (1) 70-470 mL/min (225 mL/min avg.)<br>(2) 500-1000 mL/min | 100 mL/min | 100 mL/min |
| Sampling Times: (h) | | | (1) 24 h<br>(2) 2.5-3.5 h | 20 min | 10 min |
| Sample Volumes: (L) | 1-100 L (@ 3 ppm) | 1-36 L (@ 3 ppm) | (1) 100-677 L<br>(2) 75-210 L | 2.0 L (to quantify 3.2 ppb sample) | 1.0 L |

Table 1.1: Comparison of several current methods for measuring airborne formaldehyde.

Additionally examined was analysis of the formaldehyde-TFMPH hydrazone using GC-MS with selected ion monitoring (SIM) for increased sensitivity. Oxidation of the formaldehyde-TFMPH hydrazone was investigated to account for any oxidative losses during sampling. Finally, preliminary evidence will be provided to illustrate the applicability of this TFMPH method to the measurement of other airborne aldehydes, including acetaldehyde and glutaraldehyde. The overall objectives of this work are summarized in Table 1.2.

Table 1.2: Summary of Specific Research Objectives

- Develop a new method for the measurement of airborne formaldehyde using solid phase derivatization with TFMPH, utillizing analysis by GC-ECD and/or GC-MS (SIM).
- Validate and optimize the method for parameters such as sample analysis time, sensitivity, formaldehyde-TFMPH analyte stability and solvent extraction efficiency.
- Compare the use of this TFMPH method to existing methods (DNPH and CTA) over a range of concentrations through side-by-side field sampling.
- Examine oxidation of the formaldehyde-TFMPH derivative to account for any analyte losses during sample collection.
- Show potential for applicability to other aldehydes, specifically acetaldehyde and glutaraldehyde.

*Chapter 2*

# SAMPLING PROTOCOL

## 2.1 Design of Sampling Device

Because of their portability, ease of preparation and use, solid phase extraction (SPE) cartridges were selected as solid state supports for TFMPH as opposed to the use of liquid impingers, which are more cumbersome and ill-suited to personal sampling. Initially, C-18 SPE cartridges (ENVI-18, 500 mg sorbent, 40-60 μm particle size, Supelco, Oakville ON) were used in the method development. These were later used in conjunction with silica SPE cartridges (LC-Si, 500 mg sorbent, 40-60 μm particle size, Supelco, Oakville ON).

C-18 and/or silica SPE Cartridges were dosed with 300 μL of a 99% acetonitrile, 1% $H_3PO_4$ solution containing 10 mg of TFMPH per mL. This yielded a TFMPH mass of approximately 3 mg impregnated on each cartridge. The mass of hydrazine per cartridge was derived from a similar method outlined for the dosing of C-18 and silica SPE cartridges with DNPH (Grosjean and Grosjean, 1995). Cartridges were dried in a dessicator, under vacuum, for 24 hours prior to use. The dessicator contained several Whatman #1 filter papers saturated with DNPH to act as passive collectors of formaldehyde from air within the dessicator. These filters were impregnated with DNPH by immersion in approximately 50 mL ethyl acetate containing 0.5 mL $H_3PO_4$ and saturated with DNPH. Following immersion, the filters were allowed to dry prior to placement in the dessicator. A DNPH cartridge was also attached to the vacuum valve of the dessicator as an added precaution against ambient aldehyde contamination of the cartridges. To avoid possible moisture condensation and interference, phosphorous pentoxide was included in the dessicator as a drying agent.

## 2.2 Optimization of Eluting Solvent

In validating the use of C-18 and silica SPE cartridges for the collection of airborne formaldehyde, it was necessary to determine the best solvent and elution volume for

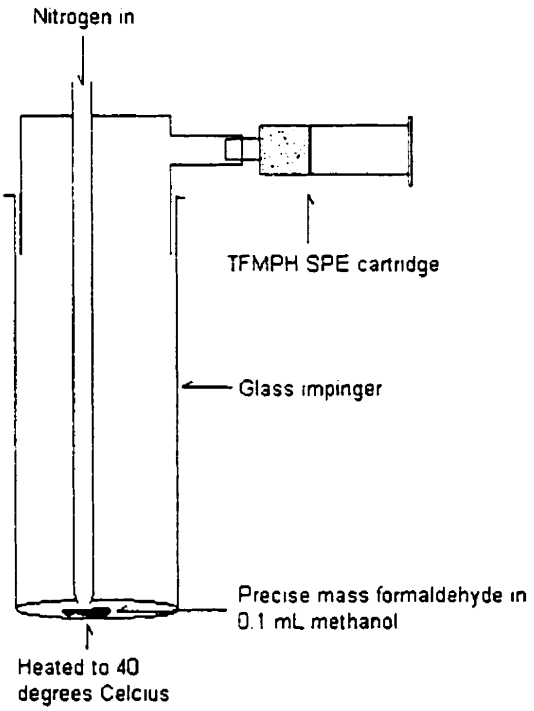


Figure 2.1: Glass impinger apparatus used to introduce gas-phase formaldehyde onto the sampling cartridges.

extraction of the formaldehyde-TFMPH derivative. The following five solvents were evaluated: acetonitrile, n-hexane, cyclohexane, toluene and ethyl acetate. These solvents were selected to reflect a range of polarities, with acetonitrile being the most polar, and cyclohexane the least polar.

To obtain the formaldehyde-TFMPH hydrazone derivative, cartridges were dosed with 100 μL of a 1.0 μg formaldehyde per μL methanol solution. This 100 μg mass of formaldehyde was introduced in the vapour phase to more closely mimic actual sampling conditions using the glass impinger apparatus depicted in figure 2.1. Following injection of the 100 μL of solution, the underlying water bath was heated to approximately 40 °C for 45 min while maintaining a steady, gentle flow of nitrogen through the impinger. Nearly complete (>97%) elution of the formaldehyde-TFMPH hydrazone derivative was achieved by eluting with 2 mL of acetonitrile, centrifuging for 2 min, eluting again with a third mL of acetonitrile and centrifuging for an additional 2 min. This was the initial elution protocol used for samples analyzed by GC-ECD. For GC-NPD analysis, it was necessary to develop a second extraction method using a non-nitrogen containing solvent. Because

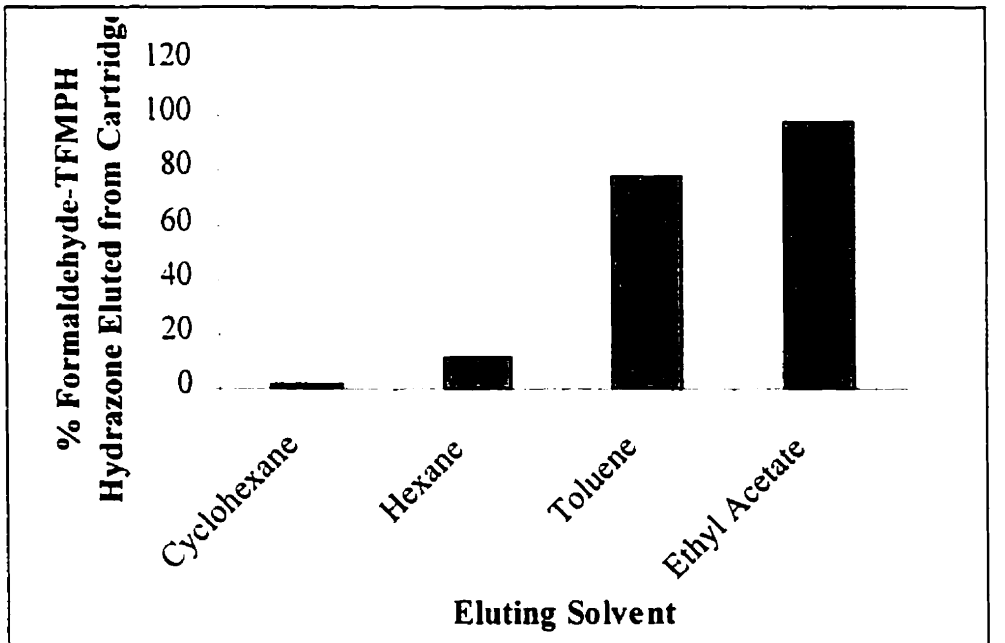


Figure 2.2: Percent formaldehyde-TFMPH hydrazone eluted from C-18 SPE cartridges by 3 mL of various solvents.

ethyl acetate was found to elute the formaldehyde-TFMPH hydrazone better than n-

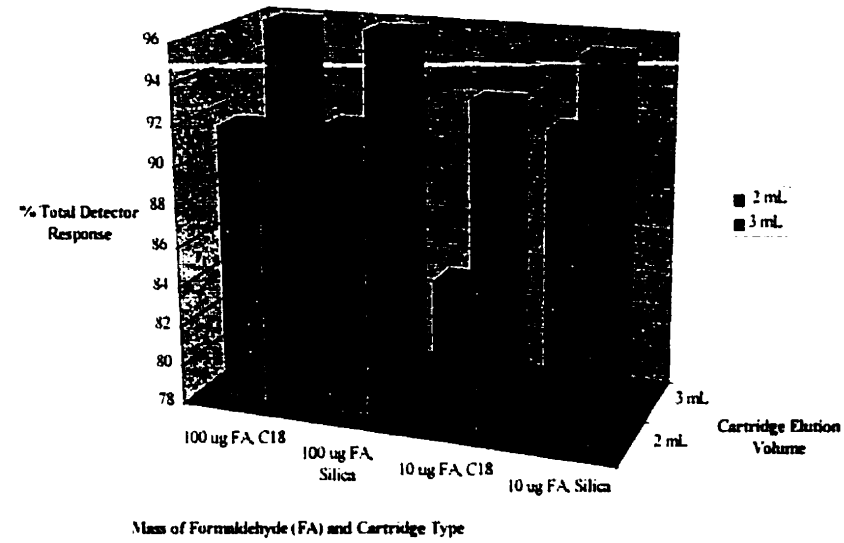


Figure 2.3: Extraction Efficiency of Ethyl Acetate, Expressed as % Total Detector Response (9/21/98)

hexane, cyclohexane or toluene (figure 2.2), it was selected for further development. Ethyl acetate was found to give a substantial (>92%) recovery of hydrazone from C-18 and silica SPE cartridges with a 3 mL elution volume (figure 2.3). As with acetonitrile, 2 mL of ethyl acetate was added initially and centrifuged through the cartridge before the addition of the third millilitre and a second centrifugation.

## 2.3 Determination of Maximum Flow Rate

Also examined was the use of differing flow rates in the collection of samples. This was necessary to ensure that no formaldehyde-TFMPH was lost from the back of the sampler

during sample collection. Four flow rates were evaluated: 250, 500, 750 and 1000 mL/min. Low-pressure-drop (Lp) Silica cartridges (360 mg sorbent, 150-250 μm particle size, Supelco, Oakville ON) impregnated with TFMPH were dosed using the glass impinger apparatus in figure 2.1. Each cartridge was dosed with 0.74 μg of formaldehyde, to simulate masses expected in occupational and/or environmental sampling. Attached in series behind each TFMPH Lp silica cartridge was a clean Lp silica cartridge to act as a trap of both TFMPH and the formaldehyde derivative, should either be lost from the front (primary) cartridge during the course of the sample collection. Samples were allowed to run for two hours at each of the four sampling flow rates. Each flow rate was evaluated in duplicate and analysis was conducted by GC-ECD using the operating conditions listed in Appendix A.

The results of this experiment indicated that flow rates up to at least 1000 mL/min can be employed without the loss of formaldehyde-TFMPH from the sampling device over a two hour sampling time. None of the four flow rates evaluated resulted in an observed peak for the formaldehyde-TFMPH derivative in the breakthrough cartridge. This indicates that, at flow rates at least as high as 1 L/min and at 25 °C, the volatility of the hydrazone analyte is sufficiently low to prevent any losses from the back of the cartridges during sample collection.

Also examined was the efficacy of the TFMPH cartridges in retaining formaldehyde. Using the vapour spiking apparatus, a DNPH cartridge was attached in series behind a TFMPH cartridge, and the system spiked with 0.74 μg of formaldehyde. The flow rate of nitrogen through the system was approximately 2 L/min, and allowed to purge for two hours. Analysis of the breakthrough DNPH cartridge revealed no additional formaldehyde-DNPH relative to the blank. This indicates that at flow rates up to approximately 2 L/min and for sampling times of at least two hours, the TFMPH Lp silica cartridges are highly effective in retaining and derivatizing formaldehyde.

## 2.4 Determination of Analytical Limits of Detection

The detection limit of the analytical procedure is defined by OSHA as the amount of analyte that can produce a peak whose height is approximately five times the height of the baseline noise (OSHA, 1998). Unfortunately, this definition of analytical detection limit cannot be easily applied to TFMPH, since baseline noise is not achieved due to formaldehyde-TFMPH present in blank samples. This high response for the analyte in the blanks was caused by formaldehyde-TFMPH present in the TFMPH as it was purchased from the supplier, which only purify the TFMPH crystals to 97%. This was confirmed by analyzing (GC-ECD, operating conditions in appendix A) a solution of TFMPH crystals without dosing onto the sampling cartridges and observing a peak for the hydrazone analyte. An added source of the high analyte background signal may have been sorption of formaldehyde from ambient air during storage of the TFMPH.

An alternate approach was taken to determine a practical limit of detection. Seven replicates of what was then believed to be at, or close to, the analytical limit of detection were run using the vapour spiking apparatus and analyzed by GC-ECD using C-18 SPE cartridges. This mass of formaldehyde was 74 ng. Seven blank samples were also eluted and analyzed by GC-ECD. These blanks were C-18 SPE cartridges that had been dosed with TFMPH and dried in the same manner as the seven cartridges which had been

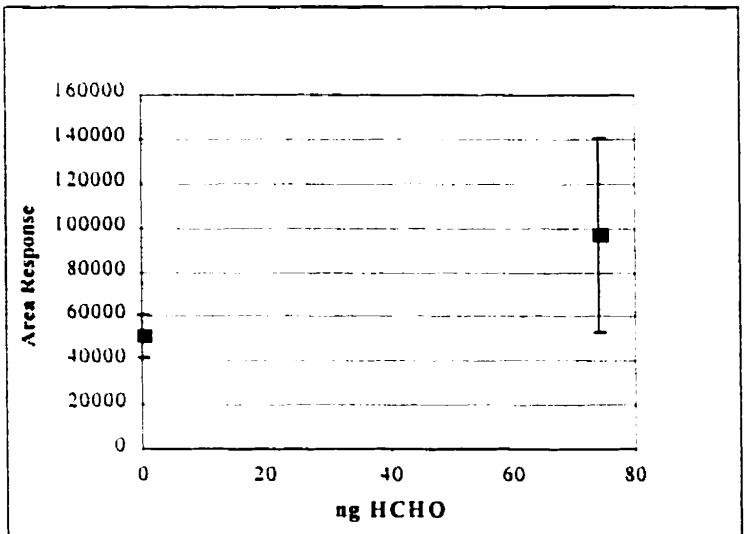

Figure 2.4: Detection limit determination for GC-ECD analysis (n=7). Error bars represent 2 standard deviations.

spiked with 74 ng of formaldehyde. All 14 cartridges were eluted with a total of 3 mL of ethyl acetate (2 mL + 1 mL). The results of this check of analytical detection limit are displayed in figure 2.4. From this data, it is possible to conclude that the detection limit of the analytical procedure is at or near 74 ng formaldehyde per sample when analysis is by GC-ECD.

In an attempt to improve (lower) the detection limit of the analytical procedure, the TFMPH crystals were recrystalized three times from hot ethanol and water. Following drying of these purified crystals under vacuum for 24 hours, they were used to prepare a TFMPH dosing solution following the procedure outlined at the start of this chapter. Following the dosing, drying, elution and analysis of C-18 SPE cartridges dosed with this solution, the chromatogram displayed in figure 2.5 (b) was obtained. Compared to 2.5 (a), which represents a blank sample before recrystalization of the TFMPH, it is clear that repeated recrystalization would lower the analytical detection limit considerably from 74 ng/sample.

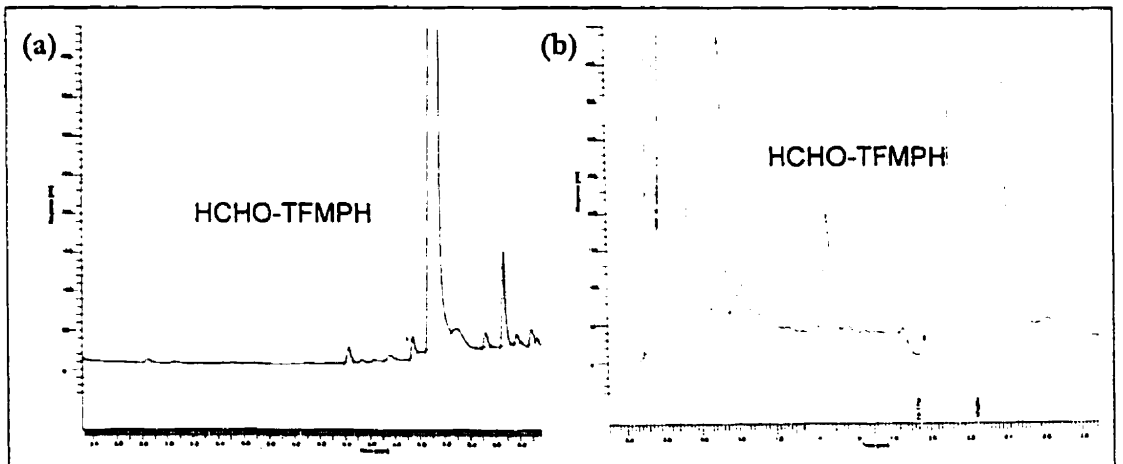


Figure 2.5: (a) GC-ECD chromatogram of pre-recrystalization blank cartridge extract (HCHO-TFMPH area response = 42460) and (b) GC-ECD chromatogram of blank cartridge extract following repeated recrystalization of TFMPH crystals to remove residual formaldehyde-TFMPH (HCHO-TFMPH area response = 22472).

1983). From the numerous failed bulk hydrazone syntheses attempted in Chapter 3, it was known that the formaldehyde-TFMPH hydrazone decomposed to form a red-coloured product. This would seem to point to the formation of a diazonium salt through a diazonium ion intermediate, which would be expected to be red in colour and which can easily be formed following oxidation of the hydrazone nitrogen (see figure 4.3). Further evidence of this mechanism through the TFMPH diazonium ion is provided by the observed formation of the phenol in 4.3(i), which would most easily be formed through $^{-}$OH nucleophilic attack at carbon $^{\#}1$ of the aromatic ring.

This decrease in TFMPH hydrazone stability relative to DNPH can be explained by the differing electron withdrawing properties of two trifluoromethyl groups in the *meta* position versus two nitro moieties in the *ortho* and *para* positions. A comparison of Hammett Sigma constants in the *para* postion ($\sigma_{para}$) yields values of 0.54 and 0.78 for trifluoromethyl and nitro moieties, respectively (Hansch *et al.*, 1995). This means that nitro groups are more electron-withdrawing than trifluoromethyl groups when substituted in the same position.

Because the T=0 fridge-stored extract was not run in replicate, it was necessary to repeat this treatment in the second stability study.

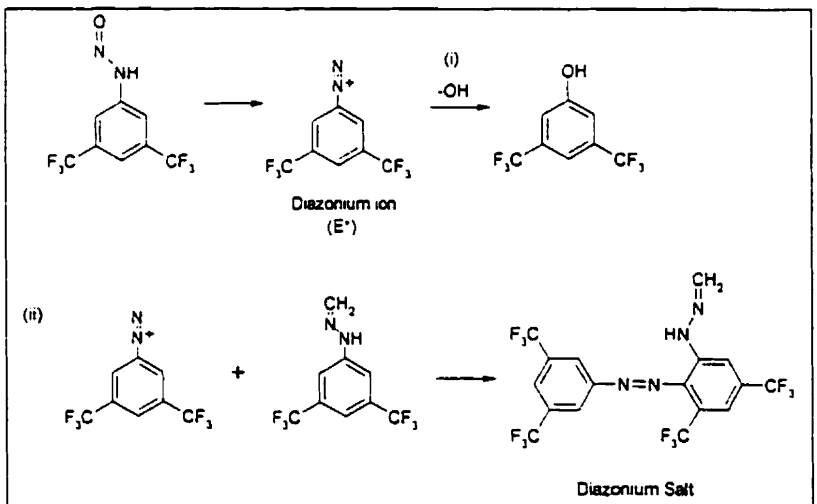


Figure 4.3: Possible oxidative degradation scheme for formaldehyde-TFMPH.

## 4.2 STABILITY STUDY #2

### Experimental

A second stability study was conducted to confirm the results of stability study #1 for the T=0 fridge-stored extracts, as well as to consider the stability of the formaldehyde-TFMPH derivative when stored in a freezer at -20 °C. To facilitate the use of higher sampling flow rates during field sampling, C-18 cartridges were abandoned in favour of silica SPE cartridges. For this reason, silica SPE cartridges were used in this second stability study. These silica SPE cartridges were dosed, extracted and analyzed in duplicate for the formaldehyde-TFMPH derivative in the same manner as described for stability study #1, with notable differences being the cartridge bonded phase and the treatments considered: (i) fridge (3 °C) storage of T=0 extracts, (ii) freezer (-20 °C) storage on silica SPE cartridges and (iii) freezer (-20 °C) storage of T=0 extracts.

A final modification incorporated into stability study #2 involved the selected elution solvent. As ethyl acetate was more likely to be used for sample elution than acetonitrile, ethyl acetate was selected for stability study #2.

### Results and Discussion

The results of stability study #2 are displayed in figure 4.4. For the fridge-stored T=0 extracts, the same trend of increasing hydrazone concentration (% Hydrazone Remaining >100%) is observed, again presumably due to sample evaporation. However, these fridge stored T=0 extracts showed very little increase in the amount of derivative over the first three days. Freezer-stored T=0 extracts showed the best stability of the three treatments considered, with very little increase or decrease observed over the 14 days for which they were examined.

Cartridges stored in the freezer appeared to show a slight decrease in the amount of derivative over the 14 day period. From this stability study, it is somewhat unclear if the hydrazone decrease observed in the freezer-stored cartridges is real, since the variability around each point (represented as 1 SD) is large enough to explain any perceived decrease in hydrazone. For this reason, a third stability study was required.

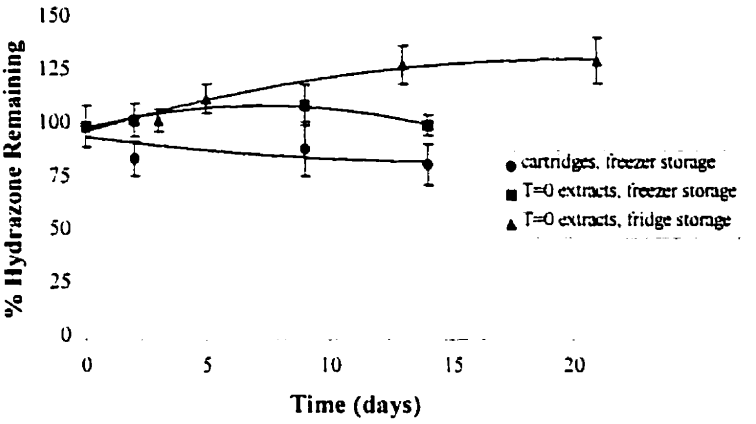


Figure 4.4: Results of formaldehyde-TFMPH hydrazone stability study #2 (error bars ± 1 SD).

## 4.3 STABILITY STUDY #3

### Experimental

Stability study #3 relied on analysis by GC-MS (SIM) and the use of an internal standard for calibration instead of the solvent peak. This was done to increase the reliability and confidence in the data generated. The internal standard selected was 2-nitro-$\alpha,\alpha,\alpha$-trifluorotoluene. This compound was selected for its easy separation from other peaks commonly observed in sample extracts and for its trifluoromethyl- moiety, hopefully

allowing it to respond in the ECD in a manner similar to TFMPH derivatives. Also examined in stability study #3 was the stability of the acetaldehyde-TFMPH derivative.

A solution of 59 μg formaldehyde and 78.8 μg acetaldehyde per 100 μL was prepared in methanol. Cartridges were dosed as described for stability study #1, then divided among the following three treatments: (i) fridge (3 °C) storage of T=0 extracts, (ii) freezer (-20 °C) storage on silica SPE cartridges and (iii) fridge (3 °C) storage on silica SPE cartridges.

Following the elution of each cartridge, 150 μL of a 0.34 mg/mL solution of internal standard was spiked into each cartridge extract. This would deliver a mass of 2-nitro-$\alpha,\alpha,\alpha$-trifluorotoluene roughly comparable to the mass of each aldehyde initially present. Analysis was conducted by GC-MS (SIM) utilizing the operating conditions displayed in appendix B.

## Results and Discussion

The results of stability study #3 are displayed in figures 4.5 and 4.6 for formaldehyde and

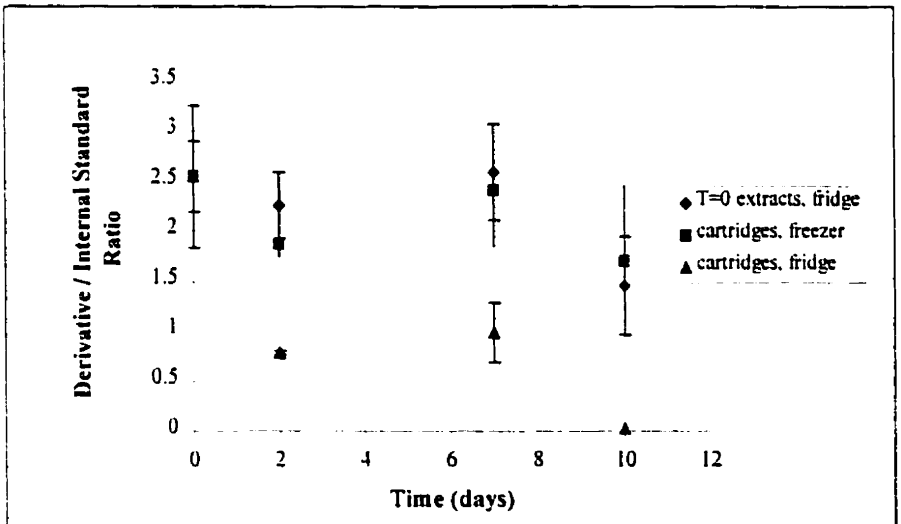


Figure 4.5: Results of formaldehyde-TFMPH stability study #3 (error bars ± 1 SD).

acetaldehyde, respectively. The lack of increase with time of the formaldehyde and acetaldehyde T=0 fridge-stored extracts for this final stability study can be explained by the storage container; unlike stability studies #1 and #2, sealed auto-sampler vials (Supelco, Oakville ON) were used instead of twist-capped vials. This would serve to cut down on the amount of solvent evaporation, and prevent any illusionary observed increase in the amount of derivative present.

No appreciable loss of the formaldehyde or acetaldehyde derivatives was observed for the first 7 days when stored on silica SPE cartridges in the freezer. For formaldehyde, this clarifies the results of stability study #2, where it was somewhat unclear whether or not a decrease had occurred in the first week.

An unexpected result was the apparent stability of the acetaldehyde-TFMPH derivative when stored on the cartridges at 3 °C. This is contrary to the results of formaldehyde-

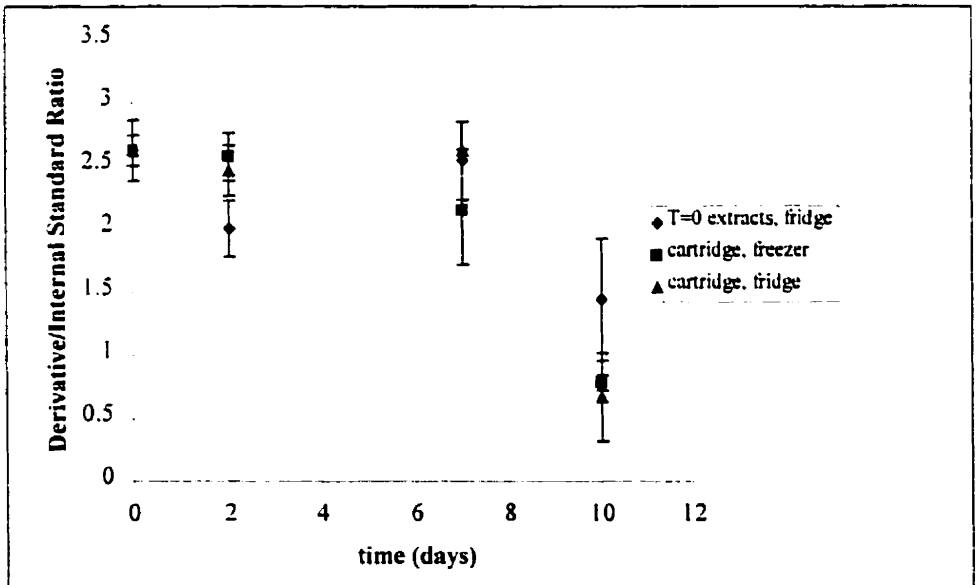


Figure 4.6: Acetaldehyde-TFMPH hydrazone stability study (error bars ± 1 SD).

TFMPH from stability studies #1 and #3.

From all three stability studies, it seemed reasonable to conclude that both formaldehyde and acetaldehyde TFMPH derivatives are stable on the sampling device for at least 7 days following sampling, provided they are kept at -20 °C or colder. Both derivatives were also stable for at least 7 days when eluted immediately and stored at 3 °C in ethyl acetate. Should storage in solution be employed, care must be taken to avoid excessive evaporation from the sample vial. This can most easily be accomplished through the use of sealed auto-sampler vials.

*Chapter 5*

# FIELD COMPARISON OF TFMPH, DNPH AND CHROMOTROPIC ACID METHODS

## Experimental

The purpose of this field sampling was to compare the use of TFMPH with two existing and accepted methods for measuring airborne formaldehyde: DNPH with analysis by HPLC-UV as specified by Koivusalmi *et al.* (1999) and CTA with analysis by visible absorbance according to NIOSH method 3500 (1994). Simultaneous field samples were collected with all three methods from a variety of indoor and outdoor environments known or suspected to contain formaldehyde. In all outdoor sampling comparisons, temperature was recorded hourly during the sampling period to allow for a correction of the sample volume. In most cases TFMPH, DNPH and CTA were sampled on different pumps due to the large difference in sampling device pressure drop and flow rate between the three methods. Use of a dual manifold for TFMPH and DNPH proved ineffective, due in part to the increase in pump failure rate which resulted. The following are the specifics of the three methods with respect to sampling, extraction, analysis and calibration.

### TFMPH

Lp Silica SPE cartridges were dosed with TFMPH and dried as described in Chapter 2. Prior to sampling, a blank cartridge was attached to an Airchek™ air sampling pump (model 224-PCXR7; SKC, Eighty Four PA) or a Buck I.H.™ pump and calibrated using a mini-Buck Calibrator (A.P. Buck Inc., Orlando FL). Flow rates employed varied from 100 to 1100 mL/min, depending on the concentration of formaldehyde expected. Following sampling, flow rates were re-measured to determine whether any significant change in sampling flow rate had occurred over the course of sample collection. Samples were

rejected if flow rates changed by more than 5%. The averages of *pre* and *post* sampling pump flow rates were used for calculating sample volumes. Cartridges were stored at -20 °C in the dark for no longer than 5 days prior to analysis. Just before the analysis, the cartridges were slowly eluted with 3 mL of ethyl acetate as described in Chapter 2. Samples were analyzed by GC-ECD and (in some cases) by GC-MS(SIM) utilizing the operating conditions provided in Appendices C and B, respectively. Both instruments were calibrated utilizing the vapour spiking technique described in Chapter 3.

DNPH

DNPH samples were collected on commercially available I.p-DNPH cartridges (Supelco). As with TFMPH, sampling pumps were calibrated before and after sample collection. Sampling flow rates varied from 70 to 1200 mL/min. Following sampling, cartridges were stored in the dark at 3-4 °C according to the prescribed sample handling instructions provided by the manufacturer (Supelco, 1997). Just prior to analysis, all samples were slowly eluted with 2 mL acetonitrile. Samples were analyzed by HPLC-UV at 360 nm using either an isocratic 70% acetonitrile to 30 % water mobile phase at 1.0 mL/min or the following gradient elution program, also at a flow rate of 1.0 mL/min:

| time (min) | 0 | 2 | 10 | 15 | 16 |
|---|---|---|---|---|---|
| % acetonitrile | 40 | 40 | 98 | 98 | 40 |

This gradient elution program was a slightly modified version of that used by Koivusalmi *et al.* (1999) for separating aldehyde-DNPH hydrazones from closely eluting hydroxyaldehyde derivatives. HPLC samples were analyzed on either a Perkin Elmer pump equipped with a model 235C diode array detector or a Varian 9010 pump equipped with a Varian 9050 Variable Wavelegth UV-VIS detector. Initially, the column used was a Supelcosil™ C-18 reversed phase column (25 cm x 4.6 mm, 5 µm particle size, Supelco). This column was

later substituted in favour of an Alltima™ C-18 end-capped column (25 cm x 4.6 mm, 5 µm particle size, Alltech), which was found to provide greater resolution.

CTA

Chromotropic acid samples were collected exactly as outlined in NIOSH method 3500 (1994). Briefly, samples were collected in glass impingers containing 20 mL of a 1% sodium bisulphite solution to stabilize the collected formaldehyde. Following sampling, aliquots from each sample impinger were reacted with chromotropic acid and sulphuric acid and the resultant purple colour measured using a Perkin Elmer model 55B spectrophotometer at 580 nm.

The CTA method is subject to several well documented interferences from phenols (Miksch *et al.*, 1981), ethanol and higher molecular weight alcohols (Sleva, 1965). For this reason, CTA was not applied to environmental sampling situations, since these interfering compounds would be present at relatively high ratios with formaldehyde, thereby invalidating the data.

For all outdoor environmental samples, temperature was recorded hourly throughout the course of sampling and used to correct the sample volume according to the ideal gas law. For samples collected indoors, the temperature was assumed to vary little from 25 °C, and therefore no volume correction was performed.

Formaldehyde-TFMPH Oxidation Experiments

Following some of the difficulty encountered with TFMPH at low (environmental) concentrations of formaldehyde (see Results and Discussion below), additional sampling was conducted to examine the degradation of formaldehyde-TFMPH during sampling. The specific design of each of these experiments is presented along with the major findings in the Results and Discussion section of this chapter.

## Results and Discussion

The results from the first six days of sampling, including samples from embalming and

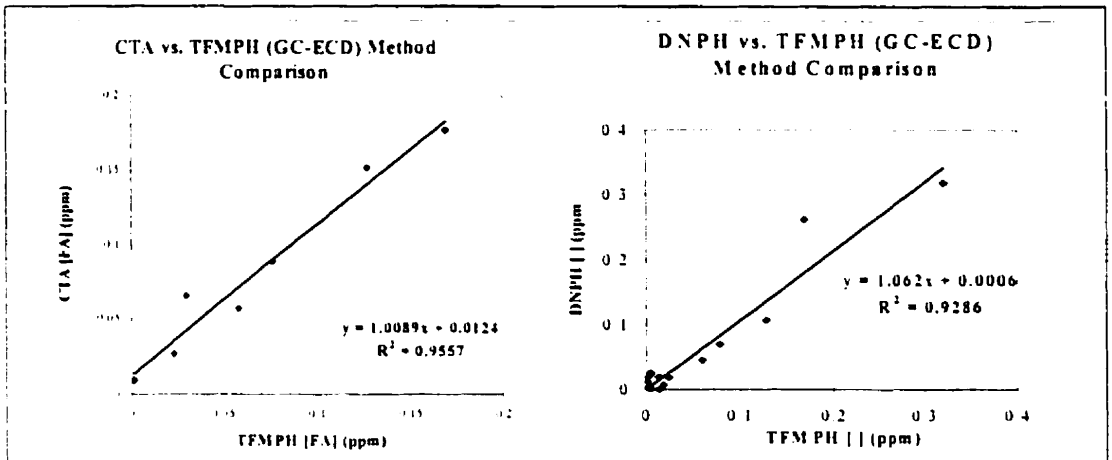


Figure 5.1: Results of first six days of sampling for CTA and DNPH vs. TFMPH.

environmental tobacco smoke exposure, are displayed in Figure 5.1 for CTA and DNPH versus TFMPH (n=7 and n=20, respectively). Both methods correlate well with TFMPH over the entire concentration range examined, with a slight 1% positive bias in the case of CTA. This positive bias is greater for DNPH at roughly 6%. While the slope in both cases is close to 1.0 and both intercepts are close to the origin, this situation does not persist when the DNPH vs. TFMPH data is examined in greater detail at formaldehyde concentrations lower than 25 ppbv (Figure 5.2). Since this is within the range of formaldehyde concentrations likely to be encountered in ambient environmental samples, the applicability of the TFMPH method at low-end environmental levels hinges on the ability to resolve this lack of agreement to the widely endorsed use of DNPH.

To examine the cause of this lack of agreement between DNPH and TFMPH at formaldehyde concentrations less than 25 ppbv, several avenues were pursued. Initially, it was thought that this lack of agreement may have been caused by a problem with the DNPH analysis, which for the first six days of sampling consisted of the isocratic 70:30

acetonitrile:water mobile phase. In the scientific literature, the application of DNPH to environmental determination of carbonyls is split almost evenly among the use of isocratic elution and gradient elution programs. It was felt that if interfering compounds were co-eluting with the formaldehyde-DNPH hydrazone while using an isocratic mobile phase, then such an interference would impact the reliability of the DNPH data at lower levels. Moreover, this would explain why at higher concentrations of HCHO, the agreement improved between the two methods.

To address these concerns, it was necessary to switch to the gradient elution program outlined in the experimental section of this chapter. Also, the column was changed from the Econosil™ C-18 (Supelco) to the Alltech Alltima™ end-capped C-18 column. The Alltech column was found to provide tighter peak widths, even in the context of greatly

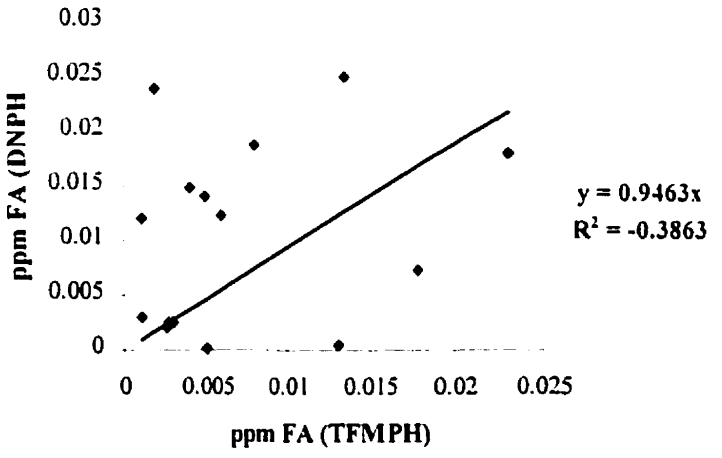


Figure 5.2: Results from Figure 5.1 for DNPH vs. TFMPH method comparison at [HCHO] < 25 ppbv, y-intercept forced through zero.

increased analysis times (from approximately 6 min running isocratic compared to 16 min with the gradient elution) when using the gradient program.

Using the gradient elution to analyze all DNPH samples, a systematic error in favour of DNPH was observed. This systematic error is illustrated by the results from the outdoor

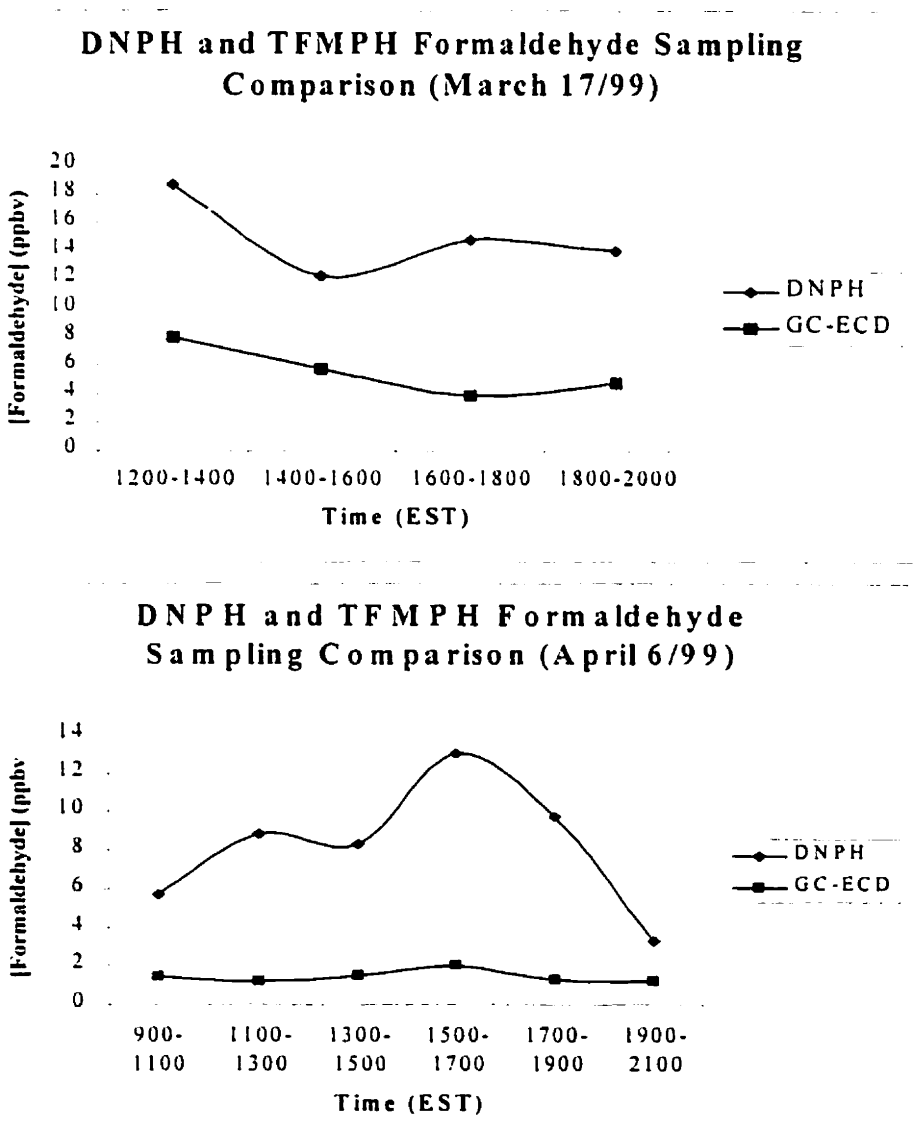


Figure 5.3: March 17th and April 6th 1999 environmental sampling comparison of DNPH to TFMPH for measurement of airborne HCHO.

environmental sampling conducted on March 17th and April 6th, 1999 (Figure 5.3). In both cases and for all samples collected, use of TFMPH with analysis by GC-ECD yields a lower concentration of formaldehyde than does DNPH.

To test the hypothesis that the formaldehyde-TFMPH hydrazone may oxidize on the sampling device following its formation, an additional examination was conducted using the nearly pure hydrazone derivative, the synthesis of which was described in Chapter 3. Oxidation of the analyte had been suspected from the bulk synthesis, where it was necessary to perform the reaction under nitrogen to prevent the formation of oxidized degradation products. The identity of oxidation products had been partially confirmed in Chapter 3. Based on the initially encouraging results presented in Figure 5.1, it was thought that oxidation may not have been significant on the sampling cartridges. At lower concentrations and in the presence of oxidants (expected in the troposphere), this assumption appears to be erroneous. To test this, approximately 2 µg of the synthesized hydrazone was loaded onto cartridges, dried with $N_2$ then either eluted immediately or having outdoor urban air drawn through at 1000 mL/min for 15, 30 or 120 min prior to elution. All sample treatments were performed in duplicate.

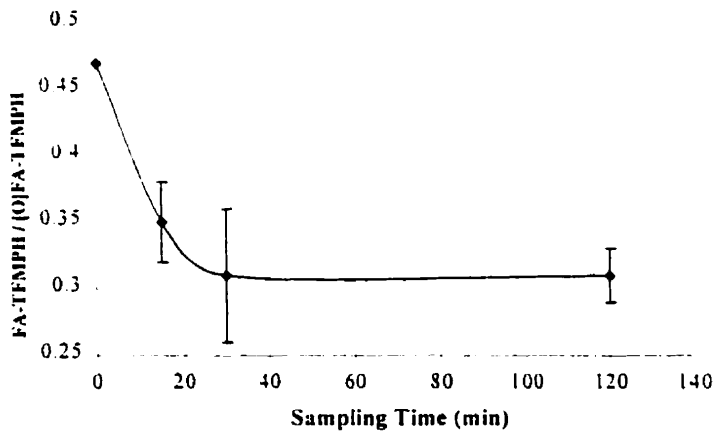


Figure 5.4: Results of formaldehyde-TFMPH hydrazone oxidation experiment.

The results of this experiment are displayed in Figure 5.4. A somewhat unexpected observation was the ease with which the hydrazone can be oxidized. Even *before* air was drawn through the cartridges, the simple process of loading the hydrazone

onto the samplers and drying off the EtOAc solvent with $N_2$ (not UHP grade, therefore likely to contain trace amounts of $O_2$) was sufficient in producing a significant oxidized product peak at time=0 min (see figure 5.5 chromatogram). It is important to note that when the synthesized hydrazone was injected onto the GC-MS without loading onto a cartridge, no peak was observed for the oxidized hydrazone degradation product. While loading the hydrazone onto the sampling

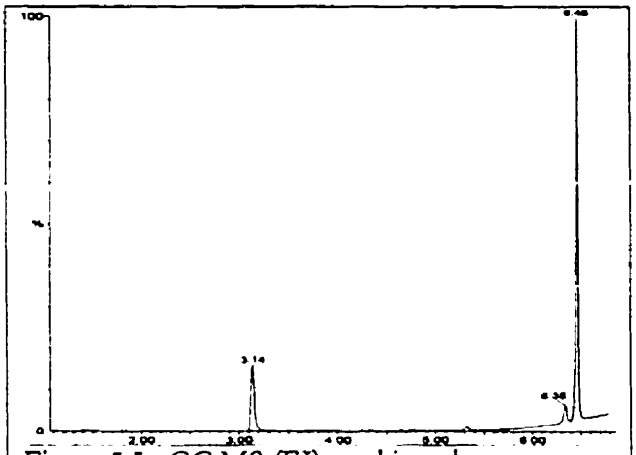

Figure 5.5: GC-MS (EI) total ion chromatogram of t=15 min point from hydrazone oxidation experiment presented in figure 5.4.

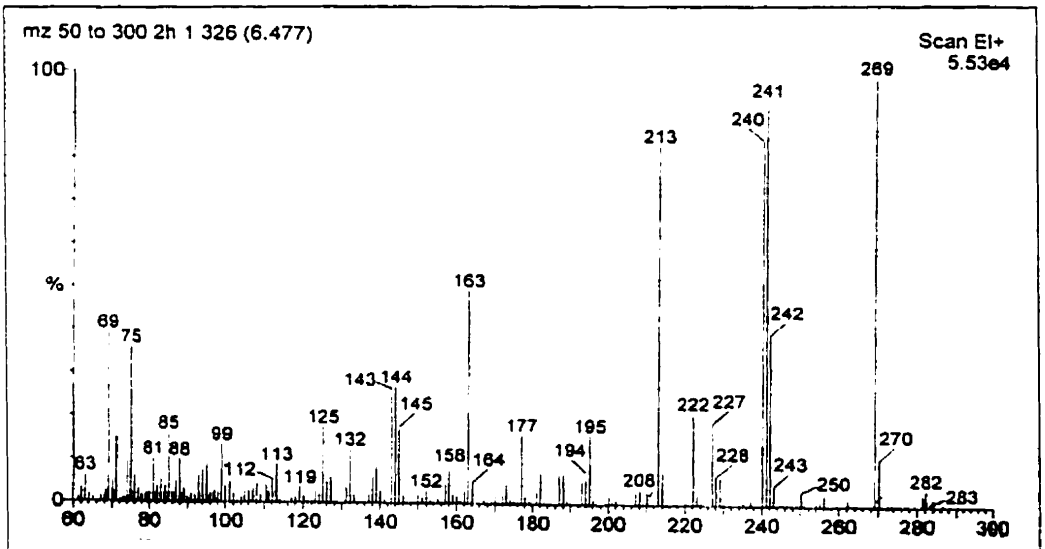


Figure 5.6: GC-MS (EI) fragmentation pattern of the oxidized formaldehyde-TFMPH degradation peak, 6.46 min in figure 5.5.

cartridges and removing the solvent with $N_2$ caused oxidation to occur, additional loss of hydrazone was observed over the first 30 min of drawing air through the samplers. Strange, however, was the lack of hydrazone loss from 30 to 120 min. This 'leveling off' of

the amount of hydrazone seems to also reflect what was observed in figure 5.3, where very little change was observed over the course of both days using TFMPH, while DNPH tended to vary more widely.

The MS fragmentation pattern for the oxidation product itself is displayed in Figure 5.6. While it is not believed that any molecular ion was observed, the ion at m/z 270 would seem to indicate oxidation. To overcome this, potassium iodide scrubbers were used in an attempt to remove any ozone which may have been responsible for the oxidation of the hydrazone. These ozone scrubbers are commercially available, and their use is well documented for the elimination of the ozone interference observed with DNPH at concentrations of formaldehyde and ozone representative of urban environments (5 ppbv HCHO, 120 ppbv ozone) (Kleindienst *et al.*, 1998). It was thought that perhaps, given the easily oxidized nature of the formaldehyde-TFMPH hydrazone, the negative ozone interference observed for DNPH at relatively high ozone concentrations became significant for TFMPH at lower concentrations of ozone. As a check of this hypothesis, four outdoor 2 hour simultaneous TFMPH samples were collected at 1000 mL/min, two with KI scrubbers and two without. A DNPH sample was also collected. The results of this check are displayed in Figure 5.7. While it may initially appear that the use of KI traps did yield a small increase in the amount of hydrazone detected in the GC-ECD analysis, this difference was not statistically

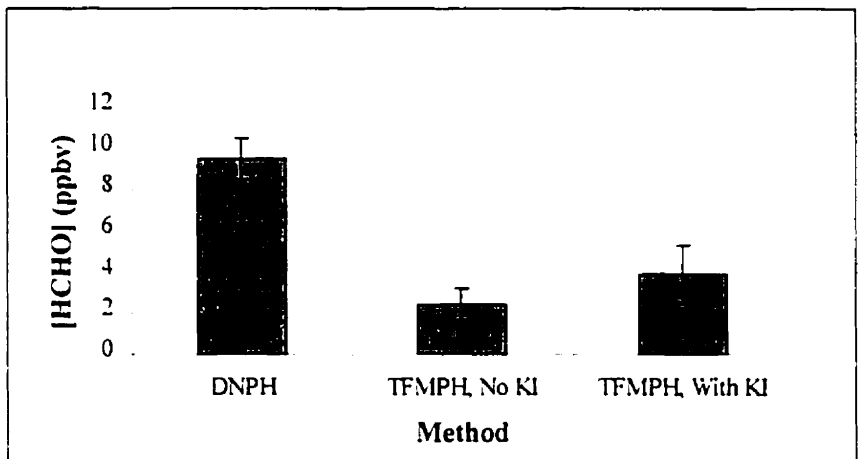


Figure 5.7: Method comparison examining the effect of adding KI ozone scrubbers to the sampling apparatus, $L_p$ silica cartridges, sampling day 11.

significant when evaluated with a t-test ($p>0.05$), nor was the slight increase sufficient to eliminate the systematic error observed.

To check whether diatomic oxygen was capable of oxidizing formaldehyde-TFMPH, 2 μg of the hydrazone was loaded onto two C-18 and two $L_p$ silica cartridges and blown to dry (approximately 15 min for each cartridge) with ultra-zero-air (Matheson, Whitby ON). The

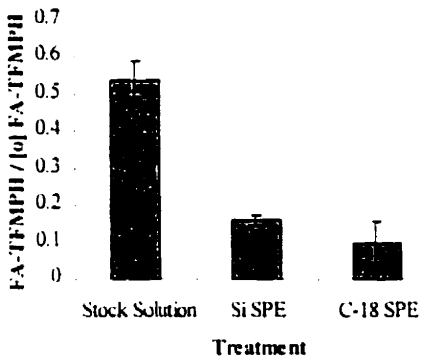


Figure 5.8: Results of ultra-zero-air experiment showing decrease in FA-TFMPH / [o]FA-TFMPH ratio following cartridge drying.

flow rate of air was approximately 1 L/min. The four cartridges were eluted with 3 mL ethyl acetate as usual, and analyzed by GC-MS (SIM). The results presented in figure 5.8 appear to confirm oxidation of formaldehyde-TFMPH by diatomic oxygen. The ratio of formaldehyde TFMPH to the oxidized formaldehyde-TFMPH product decreases following cartridge drying with zero-air.

The results of the above three experiments raise serious doubts with respect to the applicability of TFMPH to sampling airborne aldehydes, since oxidation would be expected to occur in the presence of oxygen. This data also supports the observations made during the numerous failed attempts at product purification noted in Chapter 3: the formation of oxidized degradation products following the removal of solvent from the synthesized hydrazone.

It is difficult to explain, based on the results of figures 5.3 to 5.8, why the method appears to correlate and agree with DNPH and CTA at higher airborne concentrations of formaldehyde (figure 5.1). If an oxidant as weak as diatomic oxygen were capable of oxidizing formaldehyde-TFMPH, then this oxidation would be expected to occur at all concentrations of formaldehyde. A possible explanation for this is the small number of samples at these higher airborne concentrations. Additional samples from appropriate occupational settings may reveal a systematic error as observed in figure 5.3. Alternatively, if a weak oxidant is in fact responsible for oxidation of formaldehyde-TFMPH in ambient environmental samples, then perhaps this slow rate of oxidation only becomes important at low concentrations of formaldehyde.

A final experiment was conducted to further examine the possibility of differential oxidation of formaldehyde-TFMPH on $L_p$ silica versus C-18 SPE cartridges, as well as the utility of using potassium iodide ozone scrubbers. Each sample collection treatment was repeated in triplicate for TFMPH, with two DNPH cartridges collected simultaneously. This was conducted on two separate days, with TFMPH samples analyzed by GC-ECD (operating parameters and conditions in appendix C). The results of these two sampling days are displayed in figures 5.9 and 5.10.

From figure 5.9 (a repeat of the experiment presented in figure 5.7), it is clear that sampling with TFMPH on $L_p$ silica cartridges produces a different airborne concentration of formaldehyde than DNPH. It is also apparent that the use of potassium iodide (KI)

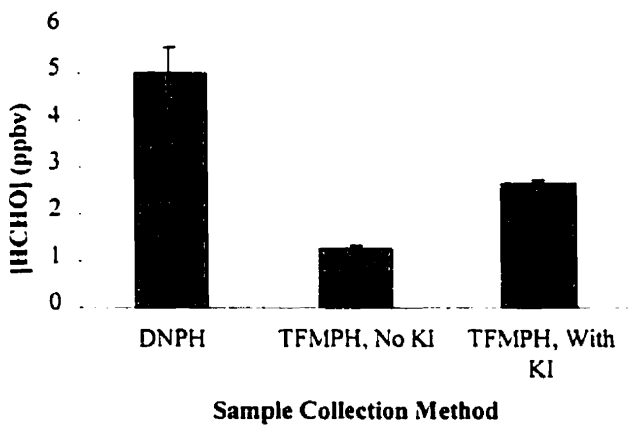


Figure 5.9: Effect of adding KI ozone scrubbers to the sampling apparatus, $L_p$ silica cartridges, sampling day 12.

scrubbers increases the amount of formaldehyde recovered, presumably by limiting the oxidation of the analyte by ozone.

Less clear are the results displayed in figure 5.10. This lack of clarity is largely the result of high variability in the use of TFMPH on C-18s, both with and without the use of KI. A possible explanation is that all TFMPH samples were within 20% of the blank value. This is really below the quantitative capacity of the method, and therefore can be regarded as unreliable. Given the magnitude of uncertainty surrounding the two TFMPH sample collection treatments, it is not possible to say with certainty whether the use of KI scrubbers had an impact on the concentration of formaldehyde measured in figure 5.10. This may in fact be more a reflection of the sampling time; while the samples in figure 5.9 were collected from 11 a.m. to 2 p.m., the samples in figure 5.10 were taken from 8 to 11 p.m. when the concentration of ozone would likely be lower.

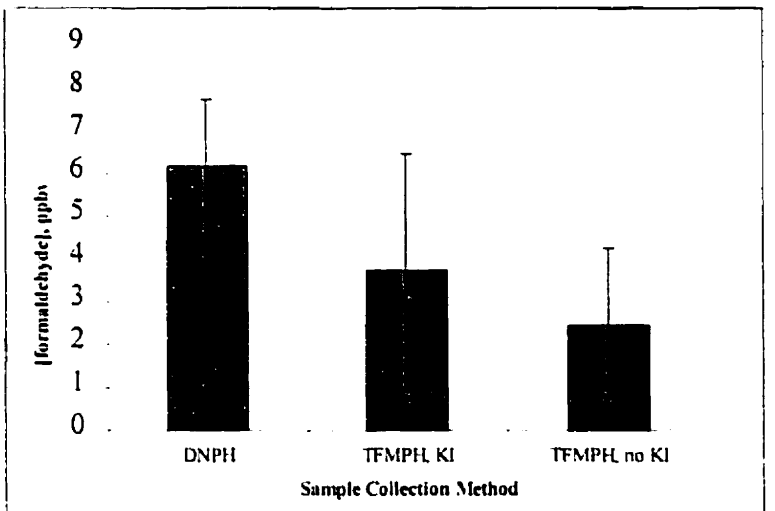

Figure 5.10: Effect of KI ozone scrubbers on formaldehyde sampling with TFMPH on C-18 SPE cartridges (n=2, sampling day 13).

There is an obvious need to reconcile the data presented in the later part of this chapter related to degradation of formaldehyde-TFMPH and the analyte stability data presented in Chapter 4. In fact, there is no contradiction between these two data sets, since Chapter 4 did show the formaldehyde-TFMPH hydrazone to be highly unstable when stored on the sampling cartridges (both at room temperature and at 3 °C). Also, the purpose of the three

stability studies in Chapter 4 was not to examine the analyte stability during *sampling*, but rather stability on the SPE cartridges during sample *storage*. A further difference lies in the fact that to spike the cartridges in Chapter 4, nitrogen gas was passed through the impingers. In light of the easily degraded nature of the formaldehyde-TFMPH derivative, this would likely differ from actual field sampling, where atmospheric oxidants would also be passing through the sampler. Figure 5.8 shows that even diatomic oxygen is capable of oxidizing the derivative. The rapid degradation of formaldehyde-TFMPH in the presence of oxygen is further supported by the results of the bulk synthesis discussed in Chapter 3; unless performed under nitrogen and kept in solution, the synthesized hydrazone was found to rapidly degrade.

Blank and Standard Curve Correction

This problem of hydrazone oxidation in the environmental samples was eventually resolved to some extent through the use of an 'oxidation blank' which provided a correction factor for the standard curve. It was suspected that because the standard curve and blanks did not have ambient air passed through at any time, their values were artificially inflated relative to the sampling cartridges. Because the blank and standards contained residual hydrazone, this background hydrazone would not be subject to oxidation as in the case

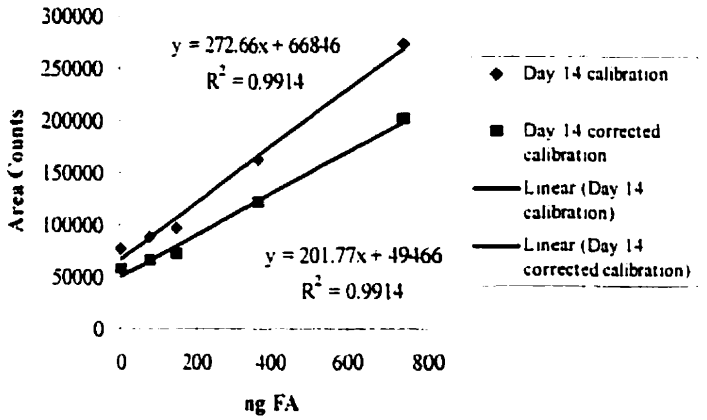


Figure 5.11: Corrected TFMPH vapour spiking standard curve incorporating oxidative loss of hydrazone during sampling.

of the field samples. The net result would be that the entire standard curve was inflated due to no oxidative loss of background hydrazone from the blank or standards.

To validate this hypothesis, an oxidation blank was run along side the samples at a flow rate of 70 mL/min for the duration of the sampling (3 hours). This blank consisted of a TFMPH cartridge connected in series behind a DNPH cartridge and a potassium iodide ozone scrubber. The DNPH cartridge was used to prevent the formation of any new formaldehyde-TFMPH hydrazone on the blank cartridge. It was hoped that the DNPH cartridge would not significantly inhibit the concentration of atmospheric oxidants other than ozone (eliminated by the KI scrubber) passing through the TFMPH cartridge. Both 'conventional' (no air drawn through, cartridges simply eluted with 3 mL EtOAc after TFMPH dosing and drying) and oxidation blanks were eluted and analyzed by GC-ECD. On average, the oxidation blanks were found to be 26% lower than the conventional blanks. Consequently, all points in the vapour spiking standard curve were lowered by 26%. This change in standard curve is illustrated in figure 5.11. When the TFMPH airborne concentration of formaldehyde is re-calculated using this corrected standard curve, the agreement between DNPH and TFMPH is improved substantially, as illustrated by figure 5.12.

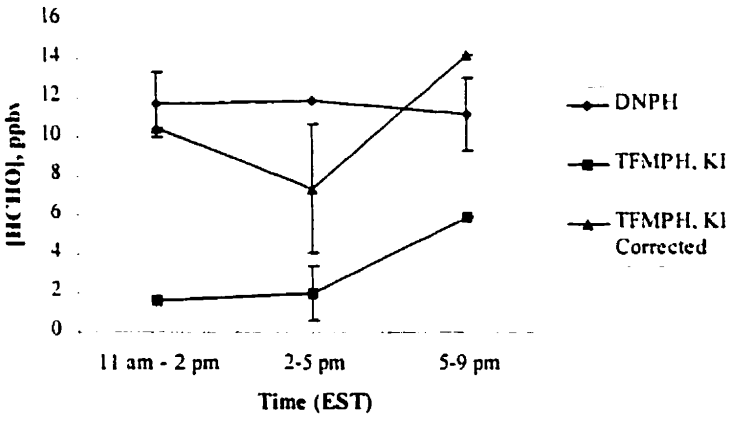


Figure 5.12: Day 14 sampling results, with and without oxidation blank correction for TFMPH on C-18 cartridges with KI scrubbers in-line.

## Conclusions

From the data presented in this chapter, it is possible to conclude that the use of TFMPH as it is presented in this thesis is suitable for environmental sampling of airborne formaldehyde, provided oxidation

of the hydrazone is accounted for with an oxidation blank as described above. Oxidation of formaldehyde-TFMPH is significant at environmental concentrations of formaldehyde. Without accounting for this oxidation through the use of potassium iodide scrubbers and an oxidation blank, the TFMPH method is systematically lower than DNPH. Unclear, however, is the reason why the method appears to perform adequately at higher, occupational concentrations without the use of potassium iodide or an oxidation blank. More sampling at formaldehyde concentrations above 25 ppbv should be performed to fully assess the method's performance at these higher, occupational levels without the use of potassium iodide scrubbers or oxidation blank. To improve the reliability of any future field sampling (either occupational or environmental), the following two blanks should be run in all cases:

1. A 'conventional blank', consisting of a TFMPH cartridge dosed and dried along with the sampling cartridges, eluted without any air being passed through
2. An 'oxidation blank' side-by-side with sample collection at a similar flow rate and for the same time period

Examining the ratio of the oxidation blank to the conventional blank yields the oxidation correction factor. This cannot be assumed to be 26% in all cases, since it will be dependent on several factors including:

1. The concentration and composition of oxidants present in the atmosphere during the sampling
2. The amount of formaldehyde-TFMPH in the blank
3. The concentration of formaldehyde present during sampling

Through the use of appropriate blanks, it appears that TFMPH provides good agreement with existing methods. The added precautions required are a direct result of the reduced stability of the formaldehyde-TFMPH hydrazone observed and discussed in Chapter 4.

*Chapter 6*

# TFMPH DERIVATIZATION OF OTHER CARBONYL COMPOUNDS

In addition to formaldehyde, a preliminary attempt was made to demonstrate the applicability of TFMPH derivatization of other carbonyl compounds. These extra compounds were acetaldehyde, benzaldehyde and glutaraldehyde. Acetaldehyde, like formaldehyde, is an aldehyde important in the chemistry of the troposphere. Glutaraldehyde is commonly used in hospitals as a sterilizing agent. While less irritating than formaldehyde, glutaraldehyde is still capable of producing acute irritation of the eyes and skin (Calder *et al.*, 1992), as well as headaches and sensitization (Axon *et al.*, 1981).

## Experimental

Four mixed standards of acetaldehyde and benzaldehyde were prepared to deliver 20, 50, 100 and 150 μg of each aldehyde in 100 μL of methanol. The vapour spiking apparatus depicted in figure 2.1 was used to introduce the aldehydes onto the sampling cartridges, C-18 SPEs dosed with TFMPH as described in Chapter 2. After 45 min to allow complete evaporation of both aldehydes, all four cartridges were eluted as described in Chapter 2 with 3 mL ethyl acetate and analyzed with GC-ECD (operating conditions in appendix A). Peak identities were confirmed by GC-MS (EI).

To examine the derivatization of glutaraldehyde, two samples were collected from a controlled chamber experiment, with the concentration in the chamber held constant at 0.1 $mg/m^3$ glutaraldehyde. Samples were collected using an Airchek™ air sampling pump

(model 224-PCXR7; SKC, Eighty Four PA) and eluted with 3 mL ethyl acetate. Analysis was conducted by GC-MS (EI).

## Results and Discussion

The standard curves obtained from the acetaldehyde and benzaldehyde calibration attempts are presented in figure 6.1. While not exceptional with respect to linearity,

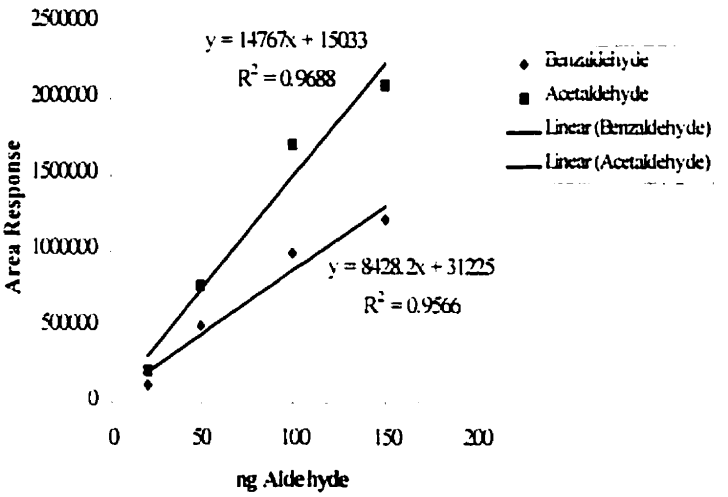


Figure 6.1: Standard Curves for benzaldehyde and acetaldehyde derivatization with TFMPH, GC-ECD.

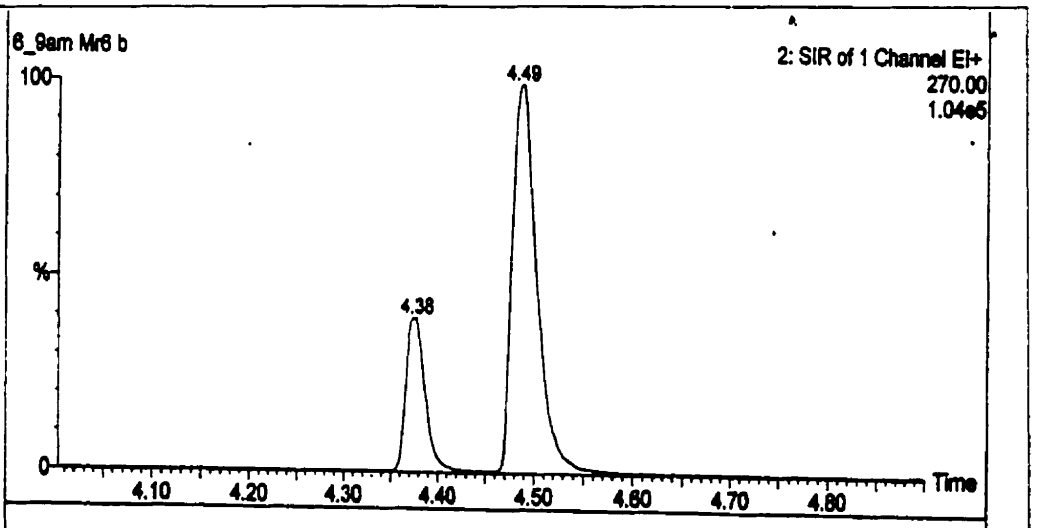


Figure 6.2: Baseline separation of *cis-* and *trans-* derivatives (4.38 and 4.40 min, respectively) formed between acetaldehyde and TFMPH. Analysis by GC-MS (SIM) at *m/z* 270.

they show that the use of TFMPH is promising for both of these carbonyl compounds. A sample GC-MS (SIM) total ion chromatogram for the acetaldehyde-TFMPH derivative is given in figure 6.2 showing baseline separation of the *cis-* and *trans-* isomers.

The GC-MS (EI) results of the glutaraldehyde chamber sampling are displayed in figure 6.3. While no molecular ion was observed for glutaraldehyde (a dialdehyde), from the ions observed it seems clear that derivatization of glutaraldehyde with TFMPH does occur. From the fragmentation pattern observed, it is possible that the derivative formed may in fact be a highly unstable seven-member ring structure, although this was not investigated any further.

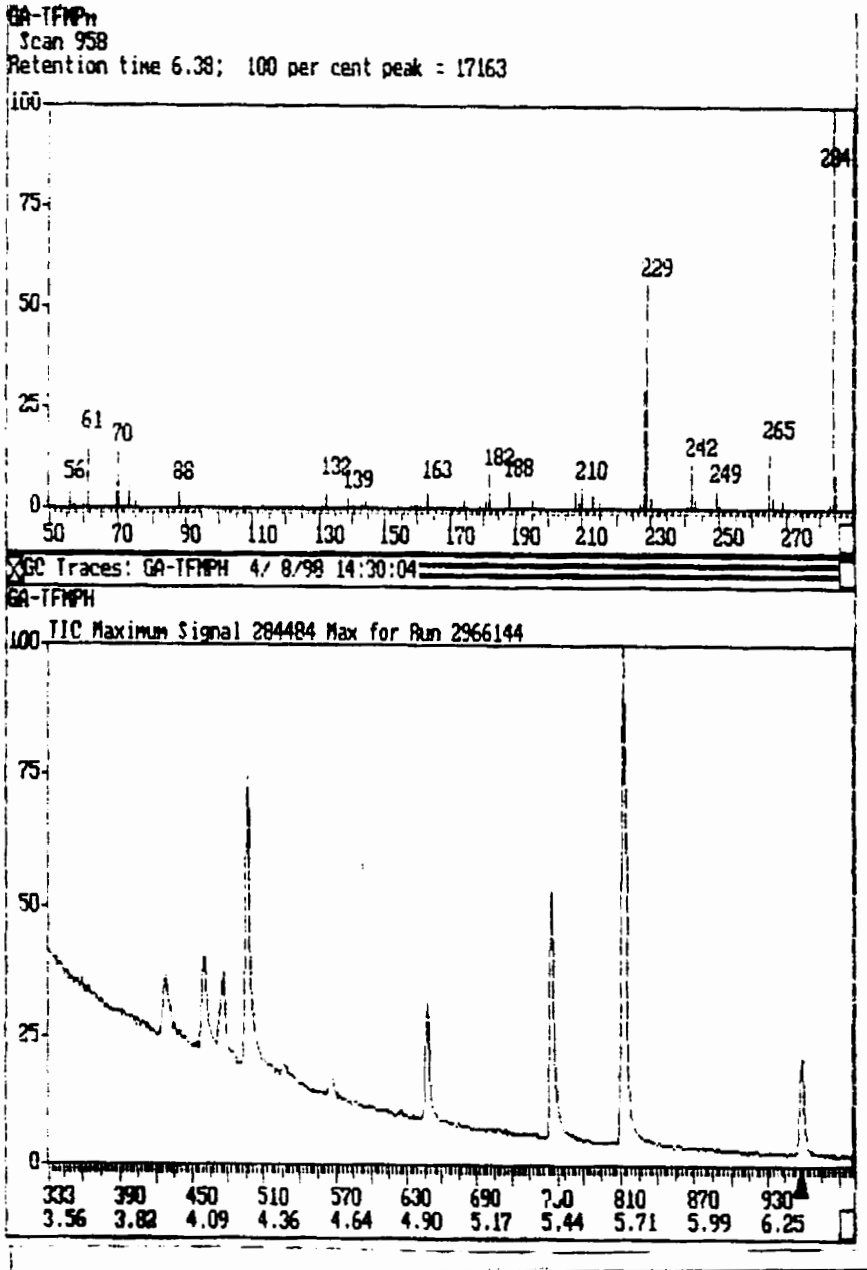


Figure 6.3: GC-MS (EI) total ion chromatogram and suspected glutaraldehyde-TFMPH derivative (6.38 min) fragmentation pattern.

*Chapter 7*

# OVERALL CONCLUSIONS AND FURTHER WORK

This work represents the first time that TFMPH has been investigated as a potential derivatizing agent for measuring airborne aldehydes. As such, numerous problems were encountered through the course of the method development. Most notably, the poor stability of the formaldehyde-TFMPH derivative through susceptibility to oxidation complicated all aspects of this work, from the synthesis of the hydrazone standard to the analysis of field samples at ambient environmental levels. In the latter case, the use of potassium iodide scrubbers to effectively remove ozone from the sampling stream and performing an oxidation blank correction effectively minimized the problem.

Overall, the TFMPH method showed good agreement with both DNPH and CTA methods at concentrations typical of occupational environments. CTA was not evaluated in ambient environmental samples and with DNPH, the agreement was less convincing at concentrations of formaldehyde less than approximately 25 ppbv. With the use of an oxidation blank, this poor agreement was likely a result of decreased precision of both TFMPH and DNPH methods at these lower concentrations.

At its current GC-ECD LOD of 74 ng formaldehyde per sample, the goal of increased sensitivity relative to existing methods was hardly realized, with the analytical sensitivity somewhere in between CTA and DNPH. Even this, however, must be taken with a disclaimer: if (as appears to be the case) the method is not effective on $L_p$ silica cartridges, then the sample collection flow rate would be limited to approximately 150 mL/min. This would in fact make the TFMPH method less sensitive overall than CTA, since the actual mass of formaldehyde collected per unit time would be greatly limited by the sampling flow rate. Regardless of the analysis technique selected, the LOD was greatly reduced from 74

ng/sample by performing repeated recrystalizations from hot ethanol as described in Chapter 2.

It has been demonstrated that TFMPH is highly reactive towards a multitude of carbonyls besides formaldehyde; acetaldehyde, acrolein, acetone, butyraldehyde, toluenaldehyde, benzaldehyde and glutaraldehyde have all demonstrated reactivity towards TFMPH on the sampling cartridges. Indeed, every carbonyl examined was shown to form the corresponding TFMPH hydrazone derivative. This high degree of TFMPH reactivity towards carbonyls opens the possibility of further developing the method as a screening tool for the measurement of multiple carbonyls simultaneously.

It is the author's opinion that, while problems do exist with the method in its current form, TFMPH as a derivatizing agent for airborne formaldehyde and other carbonyls has proven effective. TFMPH has shown itself to have distinct advantages, such as a high derivative volatility compared to other hydrazine derivatizing agents and the option of using multiple analysis techniques. At present, the possibility of using $^{19}$F-NMR for the analysis has remained unexplored; this should be pursued, as it would represent a truly novel analysis technique for airborne carbonyls and eliminate the need for component separation.

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**Appendix A:** GC-ECD Temperature Program And Operating Conditions

Detector: ECD @ 300 °C
Column: SPB-1701 (Supelco, Oakville ON), 0.32 mm x 30 m, 0.25 μm film thickness

Gases:

Carrier: $H_2$ @ 4 mL/min
ECD Make-up: $N_2$ @ 30 mL/min
Split flow: $H_2$ @ 12 mL/min (3:1 split ratio)

Injector: programmable split/splitless @ 210 °C

Oven Program:

Initial Temperature: 105 °C
Initial Hold: 2.00 min
Ramp 1: 4.0 °C/min to 112 °C, hold for 0.20 min
Ramp 2: 45.0 °C/min to 230 °C, hold for 0.2 min

Total Run Time: 6.77 min
Equilibration Time: 0.1 min

**Appendix B:** GC-MS (SIM) Temperature Program And Operating Conditions

Detector: Perkin Elmer TurboMass© Quadrupole Mass Spectrometer
Column: MDN-5 (Supelco, Oakville ON), 30 m x 0.25 mm internal diameter, 0.25 μm film thickness

Detector:

Ion Source Temperature: 180 °C
Ion Current: -70 eV

Function 1: single ion monitoring @ m/z 191 from 1.30 to 2.00 min (internal standard)

Function 2: single ion monitoring @ m/z 256 from 3.15 to 3.50 min (formaldehyde-TFMPH)

Function 3: single ion monitoring @ m/z 270 from 4.30 to 4.65 min (acetaldehyde-TFMPH)

Gases:

Carrier: $H_2$ @ 14 psig
Split flow: $H_2$ @ 25 mL/min

Injector: programmable split/splitless @ 210 °C

Oven Program:

Initial Temperature: 105 °C
Initial Hold: 2.00 min
Ramp 1: 4.0 °C/min to 112 °C, hold for 0.20 min
Ramp 2: 45.0 °C/min to 230 °C, hold for 0.2 min

Total Run Time: 6.77 min
Equilibration Time: 1.0 min

**Appendix C:** GC-ECD Temperature Program And Operating Conditions

Detector: ECD @ 300 °C
Column: SPB-1701 (Supelco, Oakville ON), 0.32 mm x 30 m, 0.25 µm film thickness

Gases:

Carrier: $H_2$ @ 4 mL/min
ECD Make-up: $N_2$ @ 30 mL/min
Split flow: $H_2$ @ 12 mL/min (3:1 split ratio)

Injector: programmable split/splitless @ 210 °C

Oven Program:

Initial Temperature: 140 °C
Initial Hold: 2.00 min
Ramp 1: 4.0 °C/min to 145 °C, hold for 0.0 min
Ramp 2: 45.0 °C/min to 260 °C, hold for 1.0 min

Total Run Time: 6.81 min
Equilibration Time: 0.1 min

**Appendix D:** Article accepted to the Journal of Chemical Education

# An Undergraduate Field Experiment for Measuring Exposure to Environmental Tobacco Smoke in Indoor Environments

**Adam M. Marsella, Scott A. Mabury, Jiping Huang and David A. Ellis**
Department of Chemistry, University of Toronto
59 St. George Street
Toronto, ON M5S 3H6

**Keywords:** analytical chemistry, environmental chemistry, chromatography, laboratory instruction

**Abstract:**

An undergraduate field experiment is described for the measurement of nicotine and various carbonyl compounds arising from environmental tobacco smoke. Students are introduced to practical techniques in HPLC-UV and GC-NPD. Also introduced are current methods in personal air sampling using small and portable field sampling pumps. Carbonyls (formaldehyde, acetaldehyde, acrolein and acetone) are sampled with solid phase extraction cartridges impregnated with 2,4-dinitrophenylhydrazine, followed by elution and analysis by HPLC-UV (360 to 380 nm). Nicotine is sampled using XAD-2 cartridges, extracted and analyzed by GC-NPD. Students gain an appreciation for the problems associated with measuring ubiquitous pollutants such as formaldehyde, as well as the issue of chromatographic peak resolution when trying to resolve closely eluting peaks. By allowing the students to formulate their own hypothesis and sampling scheme, critical thinking and problem solving are developed in addition to analysis skills. As an experiment in environmental chemistry, the application of field sampling and analysis techniques to the undergraduate lab

## Introduction

Recent public concern regarding environmental tobacco smoke (ETS) has heightened interest in estimating levels of exposure in indoor environments. A vital component in assessing exposure to ETS and likely resultant toxicities is the monitoring of tracer compounds. Nicotine is frequently employed as a marker of ETS exposure because of its specific generation from the combustion of tobacco products (*1,2*).

A frequently employed strategy for the collection of gas-phase nicotine involves sorption to an XAD resin contained in a portable sampling tube (*2,3*). Because it contains nitrogen, selective and sensitive analysis of nicotine from air samples can easily be performed using gas chromatography (GC) with nitrogen-phosphorous detection (NPD) following desorption from the sampling resin with a suitable organic solvent.

In addition to nicotine, aldehydes are also major components of ETS. A student experiment for the direct measurement of formaldehyde from cigarettes has previously been reported (*4*). Field sampling of aldehydes can be achieved through the use of derivatization with 2,4-dinitrophenylhydrazine (2,4-DNPH) impregnated onto C-18 solid phase extraction cartridges. These cartridges are commercially available, or can easily be made in the laboratory. A known volume of air is drawn through the cartridge, and the aldehydes present react selectively with the 2,4-DNPH to yield 2,4-dinitrophenylhydrazone derivatives (*5*). Once extracted, the derivatives are analyzed with high performance liquid chromatography (HPLC) with UV-vis detection (360-380 nm).

Aldehydes are commonly monitored in the workplace and indoor environment because of their acute and chronic toxicity (*6, 7*). Formaldehyde, for example, is

classified as a hazardous air pollutant by the United States Environmental Protection Agency (USEPA) (*8*). The National Institute for Occupational Safety and Health (NIOSH) classifies formaldehyde as a probable human carcinogen (*9*). This is based on epidemiological and experimental data, including the induction of squamous cell carcinomas in the nasal passages of rats and mice (*10*). Both the International Agency for Research on Cancer (IARC) and American Conference of Governmental Industrial Hygienists (ACGIH) have implicated other aldehydes including acetaldehyde and acrolein as carcinogenic (*11-13*). Acutely, aldehydes are generally regulated because of their irritant effects on the eyes, skin and upper respiratory tract (*14*).

The focus of this experiment is to familiarize students with techniques and equipment frequently employed in the measurement of gases and organic pollutants in the environment and workplace. By applying current and reliable methods for the field sampling of nicotine and aldehydes, students are able to examine the real-world problem of ETS exposure in common indoor urban environments such as bars and nightclubs. Unlike nicotine, aldehydes are not specific to the combustion of tobacco, originating from a variety of other sources including building materials and the combustion of fossil fuels (*14*). By measuring both nicotine and aldehydes, students can critically compare the use of these two methods for the estimation of ETS exposure. Finally, the experiment illustrates common variables encountered when assessing indoor ETS concentrations, including ventilation and the number of people smoking.

**Experimental Procedure**

Each group of students is supplied with two personal air sampling pumps (Buck I.H. pump; A.P. Buck, Inc.). Prior to field sampling, each pump is calibrated with a bubble flow meter. The pumps are calibrated to approximately 1000 and 500 mL/min for

nicotine and aldehydes, respectively. Students are supplied with two XAD-2 sampling cartridges (Supelco) for sampling nicotine: one for sample collection and the other to serve as a control. Similarly, each group is given two 2,4-DNPH cartridges (Supelco) for sampling aldehydes.

**Field Sampling**

Students are allowed to design a sampling strategy that they feel would test a hypothesis relevant to ETS exposure. The formulation of this hypothesis is left to the students, as is the selection of sampling location. For example, students may decide to test whether levels of nicotine and aldehydes vary significantly between smoking and non-smoking sections of a particular restaurant. In such a case, air would be drawn through the sample XAD-2 and 2,4-DNPH cartridges in the smoking section, while the control cartridges would have air drawn through them in the non-smoking section.

A summary of the sampling apparatus with the ensuing extraction and analysis is depicted in figure 1. Air is drawn through the sample and control cartridges for 1 hour, with a 15-minute warm-up period for each pump prior to the attachment of the appropriate sampling device to ensure a constant flow rate. Care is taken to ensure that the XAD-2 cartridges are fastened to the pump in the proper direction, with the secondary (breakthrough) XAD-2 section of each cartridge closest to the pump. The sampling devices are clipped to the collar of one group member to sample breathing zone air. During sampling, students are asked to note variables such as the approximate size of the room, the number of occupants smoking and any obvious lack of ventilation.

Immediately following sampling, the cartridges are capped, wrapped in aluminum foil and stored in the freezer until the time of analysis. The morning after sampling, the

flow rates of both pumps are checked again to ensure that the flow rate has remained constant.

**Laboratory Extraction and Analysis**

(i) Nicotine

The primary (sampling) sorbent section of each XAD-2 cartridge is carefully removed from the glass tube and directly placed into a separate 125 mL Erlenmeyer flask with 5 mL of ethyl acetate to extract the nicotine. Both flasks are swirled for 15 minutes. The same procedure is followed for the breakthrough section of each XAD-2 tube.

GC-NPD calibration is carried out over several orders of magnitude to accommodate the wide range of nicotine concentrations expected in the extracts. External calibration is performed using 100, 500, 1000, 2000 and 10000 pg/μL standard solutions of nicotine in ethyl acetate. Duplicate injections (1 μL) of each primary and secondary XAD-2 extract are injected onto a GC (Perkin Elmer, model??) equipped with a simplicity-1 capillary column (Supelco, 30 m x 0.32 mm internal diameter, 0.25 μm film thickness).

(ii) Aldehydes

Both DNPH cartridges are eluted with a 2 mL volume of acetonitrile. A second 2 mL of acetonitrile is passed through each cartridge and combined with the respective initial extract, yielding a total extraction volume of 4 mL for each cartridge. 5 μL of each 4 mL extract is injected into an HPLC (Perkin Elmer, model?) equipped with a Supelcosil LC-18 column (Supelco, location ZZ, 25 cm x 4.6 mm internal diameter, 5 micron particle size) and UV-vis detector (Perkin Elmer, model?). Two mixed standard

solutions of formaldehyde, acetaldehyde, acrolein and acetone are used to calibrate the wide range of concentrations expected in the samples. Although acetone is not an aldehyde, it is present in ETS (*15*) and its carbonyl group is sufficiently reactive to undergo derivatization with 2,4-DNPH, allowing for its quantification. Identifying and quantifying the acetone derivative peak is also necessitated by its close, often overlapping elution with the acrolein 2,4-DNPH derivative. Replicate injections (5, 10, 15 and 20 μL) of both the high (10 ng/μL) and low (1 ng/μL) concentration standard solutions are made onto the HPLC for external calibration.

**Results and Discussion**

Typical chromatograms of cartridge extracts and standards from GC-NPD and HPLC are displayed in figures 2 and 3, respectively. FA, AA and nicotine concentrations are listed in table 1. Poor baseline separation of acrolein and acetone made quantification of these two carbonyls difficult, with the range of class concentrations for these two compounds likely unreliable. Time limitations prevented the weakening of the mobile phase strength to allow for better chromatographic resolution between acrolein and acetone.

Most groups found detectable levels of aldehydes in their 2,4-DNPH cartridge extracts. This was likely caused by aldehydes emitted from sources other than ETS. In contrast, nicotine was only detected in 2 of the twelve groups' control XAD-2 extracts, and in both cases could be attributed to the particular control location, such as the non-smoking section of a restaurant with a non-enclosed smoking section nearby. This clearly illustrates why nicotine is usually considered a more accurate marker of ETS exposure than aldehydes, which are more ubiquitous in the environment due to multiple sources of generation.

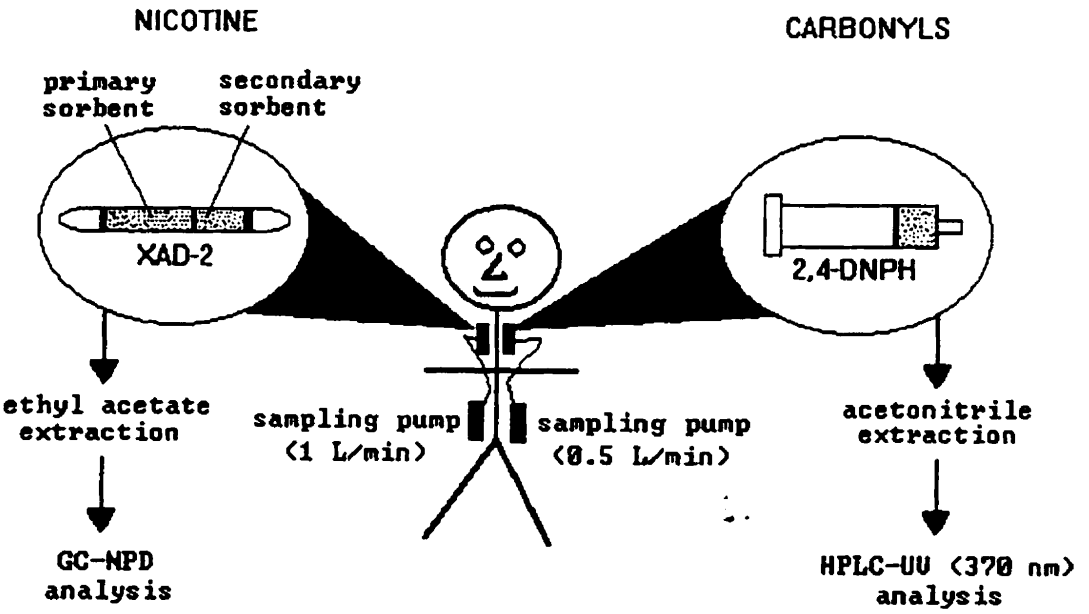
Students were not strictly limited to indoor environments. Outdoor sampling was conducted by some groups in downtown Toronto. Aldehydes were detected in these samples, likely originating from fossil fuel consumption associated with automobiles and other processes involving the incomplete combustion of organic materials. Nicotine was not detected in outdoor sampling environments, as would be expected. For groups sampling outdoors, a temperature-corrected sampling volume was calculated using the ideal gas law to compensate for the large deviations from standard temperature during sampling. Students who sampled indoors assumed a standard temperature of 25 °C when calculating airborne concentrations of carbonyls and nicotine from cartridge extract masses.

Some groups went as far as to estimate the amount of aldehydes and nicotine an individual could expect to be exposed to via inhalation over a given time period spent at their sampling location. This was done by taking the average number of breaths inspired by a resting individual per minute, and multiplying by the volume inspired per breath to yield a volume of sample air inhaled per minute while resting at the sampling location. From this information and the calculated concentrations, an estimation of inhaled aldehyde and nicotine exposure masses per unit time could be made.

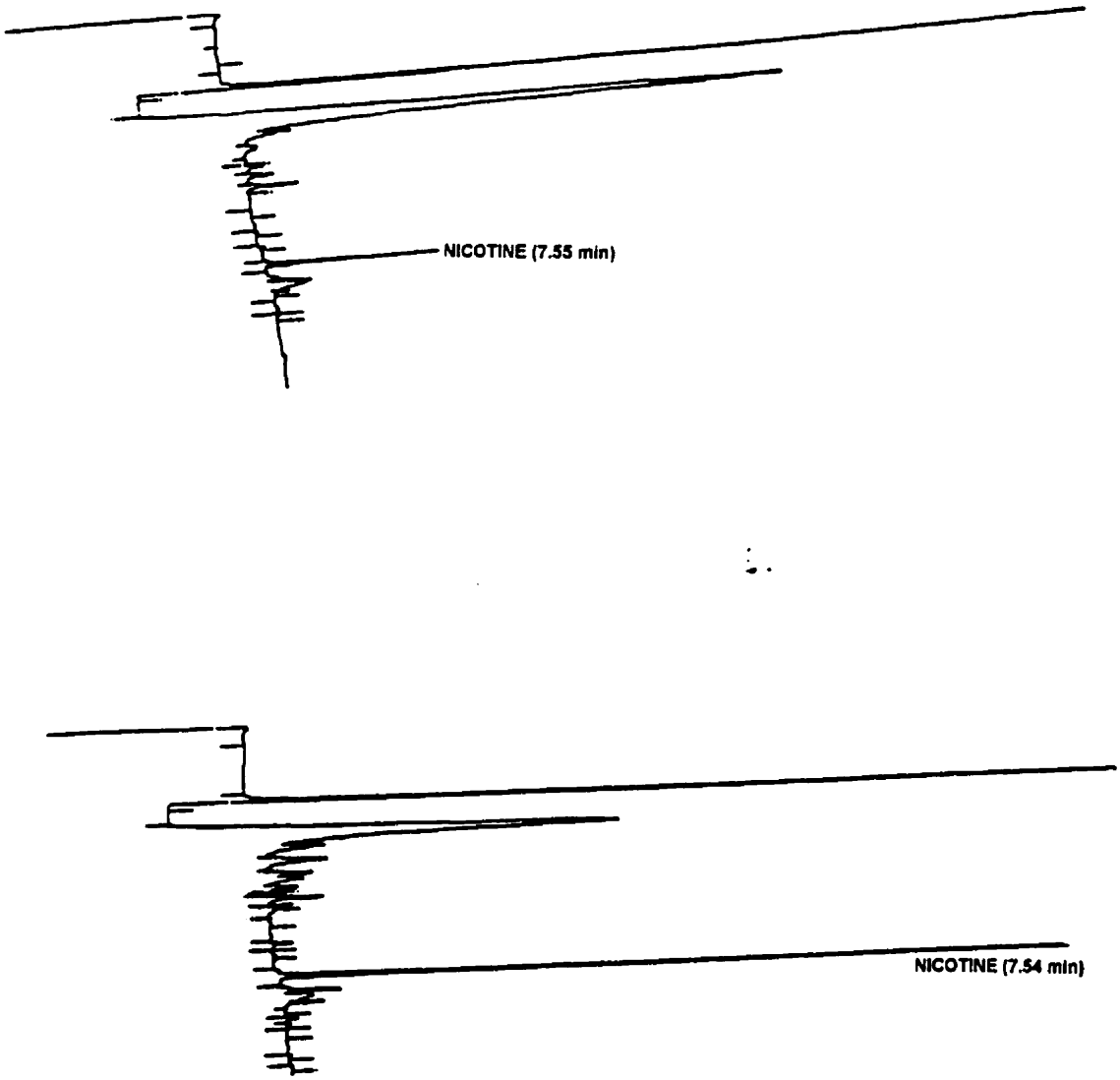
In general, students found the experiment enjoyable and worthwhile in the context of an analytical chemistry course. The freedom given in terms of choosing the sampling location and hypothesis formulation is beneficial in stimulating students to carefully think about how sampling strategies and analytical techniques apply to a real-world example related to the health of the general public. Furthermore, students gain an appreciation for the concentrations of these toxins encountered on a daily basis, and the toxicological relevance of these levels with reference to the literature.

## List of Figures

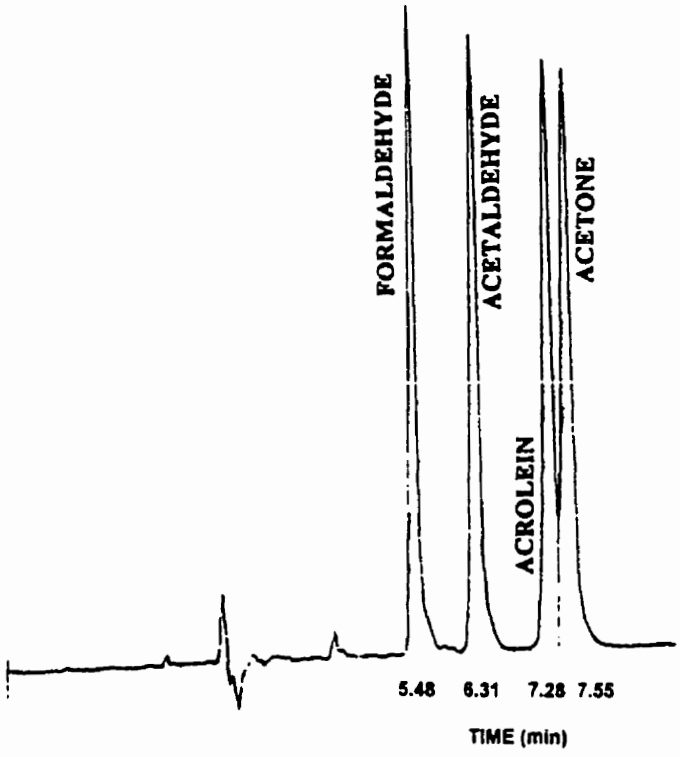
# Figure 1


NICOTINE
CARBONYLS
primary sorbent
secondary sorbent
XAD-2
2,4-DNPH
ethyl acetate extraction
sampling pump (1 L/min)
sampling pump (0.5 L/min)
acetonitrile extraction
GC-NPD analysis
HPLC-UV (370 nm) analysis

# Figure 2



(I)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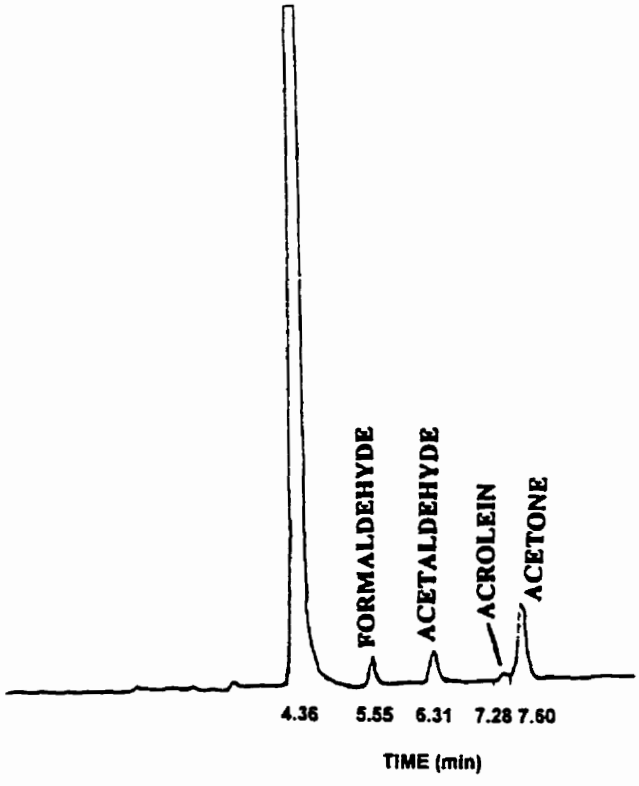
ACETALDEHYDE
ACROLEIN
ACETONE
5.48
6.31
7.28
7.55
TIME (min)

(II)


FORMALDEHYDE
ACETALDEHYDE
ACROLEIN
ACETONE
4.36
5.55
6.31
7.28
7.60
TIME (min)

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**Appendix E:** Article submitted to The International Journal of Environmental Analytical Chemistry

# 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

A. M. Marsella[1], J. T. Purdham[1] and S. A. Mabury[2*]

[1]Gage Occupational and Environmental Health Unit, Department of Public Health Sciences, University of Toronto, 223 College Street, Toronto, Ontario, Canada, M5T 1R4; [2]Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada, M5S 1A1.

*Corresponding Author:

Professor Scott Mabury
Department of Chemistry, University of Toronto
80 St George Street
Toronto, ON
Canada
M5S 3H6

tel: (416) 978-1780
fax: (416) 978-3596
e-mail: smabury@alchemy.chem.utoronto.ca

ABSTRACT

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.

**KEY WORDS:** 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 fuels and industrial processes such as smelting (1). In general, there is widespead 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 the long analysis times required in comparison to 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, 33% 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.

## EXPERIMENTAL METHODS

### *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 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 x 30 m, 0.25 μm film thickness; Supelco). The injector and detector temperatures were 210 and 300 °C, respectively. The oven was temperature programmed 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.

*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 recrystalization 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:

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

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

*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 3. 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).

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 120ppbv (20). Given that formaldehyde-TFMPH appears to be more easily oxidized than the formaldehyde-DNPH derivaitve, 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).

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 value reported for DNPH of 9 ng/sample (11). This detection limit can be improved to approximately 10 ng/sample through repeated recrystalization 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.

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 1, was 12.1 ppbv.

Analysis by GC-MS/SI M 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. 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.

## 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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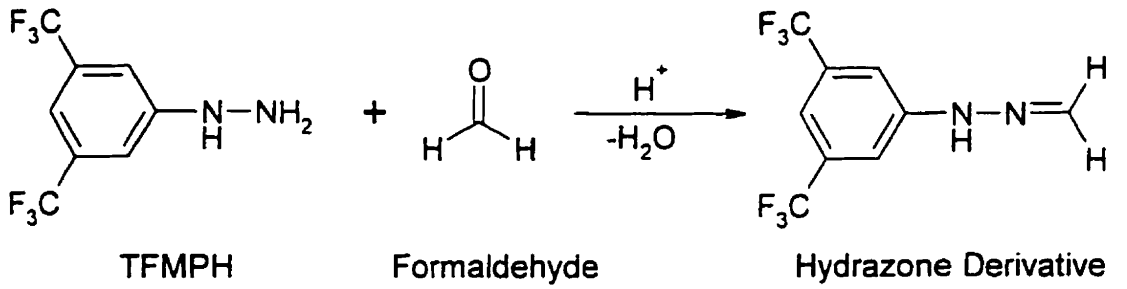


Figure 1. TFMPH structure and formaldehyde derivatization scheme.

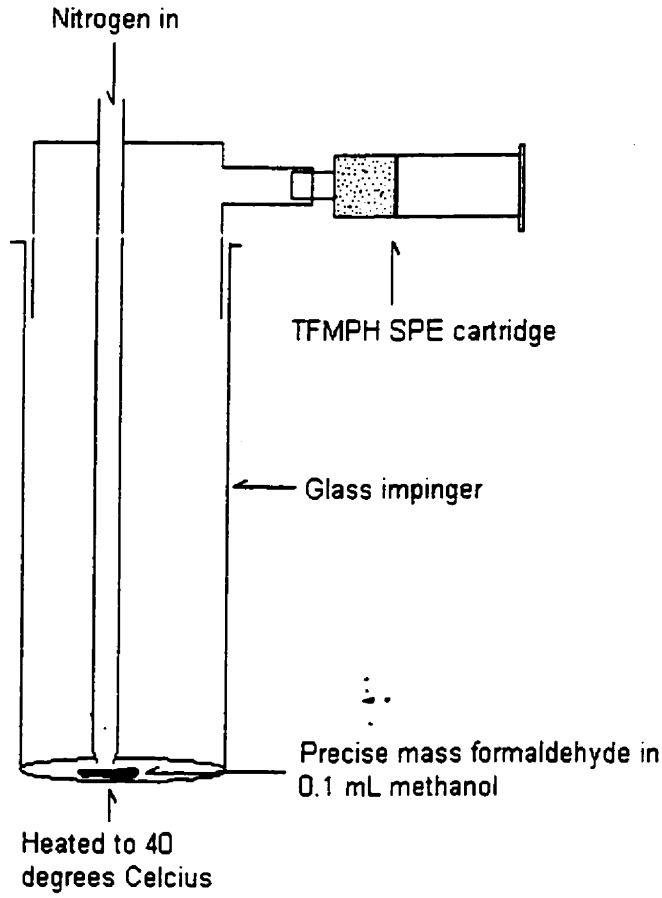


Figure 2. Vapour spiking apparatus used to spike TFMPH cartridges with known masses of formaldehyde.

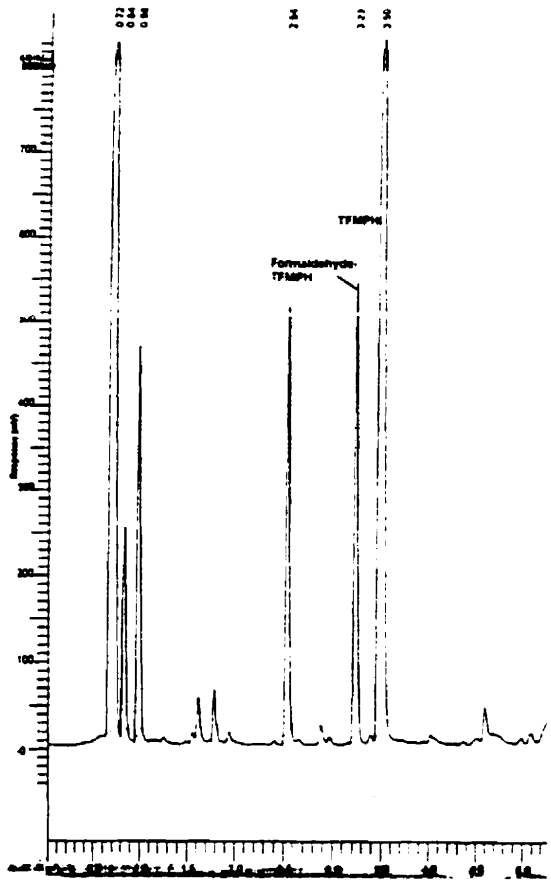


Figure 3: GC-ECD chromatogram showing TFMPH (3.5 min) and formaldehyde-TFMPH derivative (3.2 min).

**Sampling Location:** Day-long sampling from LM roof
**Date:** April 6, 1999

| Pump # | Sample I.D. | Method | Initial F.R. (l/min) | Start (min) | End (min) | Sampling Time (min) | (l/min) Final F.R. | (l/min) Avg. F.R. | Sample Vol (l) | Sample Vol (m3) | Sampl. Temp (K) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Buck1 | 9-11 am | DNPH | 0.9342 | 0 | 120 | 120 | 0.9439 | 0.93905 | 112.686 | 0.112686 | 281 |
| | | TFMPH, GC-MS | 0.9311 | 0 | 120 | 120 | 0.9065 | 0.9188 | 110.256 | 0.110256 | 281 |
| | | TFMPH, GC-ECD | 0.9311 | 0 | 120 | 120 | 0.9065 | 0.9188 | 110.256 | 0.110256 | 281 |
| Buck4 | 11 am-1 pm | DNPH | 0.8904 | 0 | 120 | 120 | 0.8959 | 0.89315 | 107.178 | 0.107178 | 284 |
| | | TFMPH, GC-MS | 1.0091 | 0 | 120 | 120 | 1.011 | 1.01005 | 121.206 | 0.121206 | 284 |
| | | TFMPH, GC-ECD | 1.0091 | 0 | 120 | 120 | 1.011 | 1.01005 | 121.206 | 0.121206 | 284 |
| Buck1 | 1-3 pm | DNPH | 0.8006 | 0 | 120 | 120 | 0.8019 | 0.80125 | 96.15 | 0.09615 | 287 |
| | | TFMPH, GC-MS | 0.8766 | 0 | 120 | 120 | 0.9031 | 0.88985 | 106.782 | 0.106782 | 287 |
| | | TFMPH, GC-ECD | 0.8766 | 0 | 120 | 120 | 0.9031 | 0.88985 | 106.782 | 0.106782 | 287 |
| Buck4 | 3-5 pm | DNPH | 0.8557 | 0 | 120 | 120 | 0.8815 | 0.8686 | 104.232 | 0.104232 | 289 |
| | | TFMPH, GC-MS | 0.8578 | 0 | 120 | 120 | 0.88 | 0.8689 | 104.268 | 0.104268 | 289 |
| | | TFMPH, GC-ECD | 0.8578 | 0 | 120 | 120 | 0.88 | 0.8689 | 104.268 | 0.104268 | 289 |
| Buck1 | 5-7 pm | DNPH | 0.7591 | 0 | 120 | 120 | 0.8101 | 0.7846 | 94.152 | 0.094152 | 289 |
| | | TFMPH, GC-MS | 1.024 | 0 | 120 | 120 | 1.033 | 1.0285 | 123.42 | 0.12342 | 289 |
| | | TFMPH, GC-ECD | 1.024 | 0 | 120 | 120 | 1.033 | 1.0285 | 123.42 | 0.12342 | 289 |
| Buck4 | 7-9 pm | DNPH | 0.766 | 0 | 120 | 120 | 0.7978 | 0.7819 | 93.828 | 0.093828 | 287 |
| | | TFMPH, GC-MS | 1.224 | 0 | 120 | 120 | 1.268 | 1.246 | 149.52 | 0.14952 | 287 |
| | | TFMPH, GC-ECD | 1.224 | 0 | 120 | 120 | 1.268 | 1.246 | 149.52 | 0.14952 | 287 |

| Temp. Corr. Vol (m3) | Tot. Mass Coll'td (mcg) | Blank Corr. Mass (mcg) | Air [ ] (mcg/m3) | Air [ ] (ppm) |
|---|---|---|---|---|
| 0.119503302 | | 0.83 | 6.945414752 | 0.005665143 |
| 0.116926292 | | | 0 | 0 |
| 0.116926292 | | 0.2 | 1.710479285 | 0.001395181 |
| 0.112461423 | | 1.21 | 10.75924502 | 0.008775958 |
| 0.127180944 | | | 0 | 0 |
| 0.127180944 | | 0.19 | 1.493934504 | 0.001218553 |
| 0.099835192 | | 1.01 | 10.11667312 | 0.008251833 |
| 0.11087469 | | | 0 | 0 |
| 0.11087469 | | 0.21 | 1.8940301 | 0.001544897 |
| 0.107477979 | | 1.71 | 15.91023587 | 0.012977449 |
| 0.1075151 | | | 0 | 0 |
| 0.1075151 | | 0.27 | 2.511275152 | 0.002048363 |
| 0.097084069 | | 1.15 | 11.84540378 | 0.009661901 |
| 0.127263529 | | | 0 | 0 |
| 0.127263529 | | 0.21 | 1.650119252 | 0.001345947 |
| 0.097424195 | | 0.4 | 4.10575627 | 0.003348929 |
| 0.155250732 | | | 0 | 0 |
| 0.155250732 | | 0.23 | 1.481474499 | 0.001208389 |

**Sampling Location:** Day-long sampling from LM roof, photolysis check
**Date:** April 12, 1999

| Pump # | Sample I.D. | Method | Initial F.R. (l/min) | Start (min) | End (min) | Sampling Time (min) | (l/min) Final F.R. | (l/min) Avg. F.R. | Sample Vol (l) | Sample Vol (m3) | Sampl. Temp (K) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Buck1 | 11-1 pm | DNPH | 0.703 | 0 | 120 | 120 | 0.726 | 0.7145 | 85.74 | 0.08574 | 280 |
| | | TFMPH, foil | 0.961 | 0 | 120 | 120 | 0.951 | 0.956 | 114.72 | 0.11472 | 280 |
| | | TFMPH, no foil | 0.988 | 0 | 120 | 120 | 0.993 | 0.9905 | 118.86 | 0.11886 | 280 |

| Temp. Corr. Vol (m3) | Tot. Mass Coll'td (mcg) | Blank Corr. Mass (mcg) | Air [ ] (mcg/m3) | Air [ ] (ppm) |
|---|---|---|---|---|
| 0.091251857 | | 0.97 | 10.62992064 | 0.008670472 |
| 0.122094857 | | 0.39 | 3.194237736 | 0.002605433 |
| 0.126501 | | 0.336 | 2.656105485 | 0.002166497 |

**Sampling Location:** Lash Miller Roof, Day 11
**Date:** March 17, 1999

| Pump # | Sample I.D. | Method | Initial F.R. (l/min) | Start (min) | End (min) | Sampling Time (min) | Final F.R. | Avg. F.R. | Sample Vol (l) | Sample Vol (m3) | Sampl. Temp (K) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Buck1 | DNPH, no KI | DNPH, HPLC-UV | 0.6569 | 0 | 120 | 120 | 0.6563 | 0.6566 | 78.792 | 0.078792 | 286 |
| Buck 4 | KI #1 | TFMPH, GC-ECD | 0.8594 | 0 | 120 | 120 | 0.8431 | 0.85125 | 102.15 | 0.10215 | 286 |
| Buck 4 | KI #2 | TFMPH, GC-ECD | 1.077 | 0 | 120 | 120 | 1.082 | 1.0795 | 129.54 | 0.12954 | 286 |
| Buck1 | no KI #1 | TFMPH, GC-ECD | 0.9744 | 0 | 120 | 120 | 0.9426 | 0.9585 | 115.02 | 0.11502 | 286 |
| Buck 2 | no KI #2 | TFMPH, GC-ECD | 1.057 | 0 | 120 | 120 | 1.058 | 1.0575 | 126.9 | 0.1269 | 286 |

| Temp. Corr. Vol (m3) | Tot. Mass Coll'td (mcg) | Blank Corr. Mass (mcg) | Air [ ] (mcg/m3) | Air [ ] (ppm) |
|---|---|---|---|---|
| 0.082097958 | 0.953 | 0.953 | 11.60808408 | 0.009468327 |
| 0.106436014 | 0.642 | 0.642 | 6.031792961 | 0.004919932 |
| 0.134975245 | 0.476 | 0.476 | 3.526572601 | 0.002876508 |
| 0.119846014 | 0.439 | 0.439 | 3.6630338 | 0.002987815 |
| 0.132224476 | 0.299 | 0.299 | 2.261306001 | 0.001844472 |

**Avg (KI):** 0.003898
**std. Dev (KI):** 0.001445
**Avg (no KI):** 0.002416
**std. Dev (no KI):** 0.000808

**Sampling Location:** LM roof, Day 12, Oxidation check (another one)
**Date:** April 28, 1999

| Pump # | Sample I.D. | Method | Initial F.R. (l/min) | Start (min) | End (min) | Sampling Time (min) | (l/min) Final F.R. | (l/min) Avg. F.R. | Sample Vol (l) | Sample Vol (m3) | Sampl. Temp (K) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Buck 1 | Sup. DNPH 1 | DNPH | 1.193 | 0 | 180 | 180 | 1.17 | 1.1815 | 212.67 | 0.21267 | 286 |
| | Sup. DNPH 2 | DNPH | 0.9675 | 0 | 180 | 180 | 0.9753 | 0.9714 | 174.852 | 0.174852 | 286 |
| Buck 4 | H.M. DNPH 1 | DNPH | 0.7463 | 0 | 180 | 180 | 0.7409 | 0.7436 | 133.848 | 0.133848 | 286 |
| | H.M. DNPH 2 | DNPH | 1.205 | 0 | 180 | 180 | 1.2313 | 1.21815 | 219.267 | 0.219267 | 286 |
| SKC-15186 | C18 w/o KI 1 | TFMPH | 0.0432 | 0 | 180 | 180 | 0.04273 | 0.042965 | 7.7337 | 0.0077337 | 286 |
| | C18 w/o KI 2 | TFMPH | 0.0481 | 0 | 180 | 180 | 0.04637 | 0.047235 | 8.5023 | 0.0085023 | 286 |
| SKC-9902 | C18 KI 1 | TFMPH | 0.0604 | 0 | 180 | 180 | 0.0581 | 0.05925 | 10.665 | 0.010665 | 286 |
| | C18 KI 2 | TFMPH | 0.0602 | 0 | 180 | 180 | 0.0572 | 0.0587 | 10.566 | 0.010566 | 286 |
| SKC-95 | Si w/o KI 1 | TFMPH | 0.5959 | 0 | 180 | 180 | 0.6037 | 0.5998 | 107.964 | 0.107964 | 286 |
| | Si w/o KI 2 | TFMPH | 0.7725 | 0 | 180 | 180 | 0.7827 | 0.7776 | 139.968 | 0.139968 | 286 |
| SKC-15193 | Si KI 1 | TFMPH | 0.6497 | 0 | 180 | 180 | 0.6433 | 0.6465 | 116.37 | 0.11637 | 286 |
| | Si KI 2 | TFMPH | 0.644 | 0 | 180 | 180 | 0.6426 | 0.6433 | 115.794 | 0.115794 | 286 |

| Temp. Corr. Vol (m3) | Tot. Mass Coll'td (mcg) | Blank Corr. Mass (mcg) | Air [ ] (mcg/m3) | Air [ ] (ppm) |
|---|---|---|---|---|
| 0.221593217 | | 1.46 | 6.588649333 | 0.005374142 |
| 0.182188448 | | 1.03 | 5.653486891 | 0.004611361 |
| 0.139464 | 0.837 | 0.717 | 5.141111685 | 0.004193433 |
| 0.228467014 | 1.54 | 1.42 | 6.215339253 | 0.005069645 |
| 0.008058191 | | 0.039 | 4.839795984 | 0.00394766 |
| 0.00885904 | | 0.008 | 0.903032397 | 0.000736573 |
| 0.011112483 | | | 0 | 0 |
| 0.011009329 | | | 0 | 0 |
| 0.112493958 | | 0.162 | 1.440077341 | 0.001174623 |
| 0.145840783 | | 0.233 | 1.597632671 | 0.001303136 |
| 0.121252657 | | 0.384 | 3.166940902 | 0.002583168 |
| 0.12065249 | | 0.405 | 3.356747976 | 0.002737987 |

**Sampling Location:** LM roof, Day 13, Oxidation check (#3), 8 pm-11 pm
**Date:** May 4, 1999

| Pump # | Sample I.D. | Method | Initial F.R. (l/min) | Start (min) | End (min) | Sampling Time (min) | (l/min) Final F.R. | (l/min) Avg. F.R. | Sample Vol (l) | Sample Vol (m3) | Sampl. Temp (K) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Buck 4 | DNPH #1 | DNPH | 0.553 | 0 | 175 | 175 | 0.55 | 0.5515 | 96.5125 | 0.0965125 | 292 |
| | DNPH #2 | DNPH | 0.508 | 0 | 175 | 175 | 0.513 | 0.5105 | 89.3375 | 0.0893375 | 292 |
| SKC-36 | KI #1 | TFMPH on C-18 | 0.0663 | 0 | 175 | 175 | 0.102 | 0.08415 | 14.72625 | 0.01472625 | 292 |
| | no KI #1 | TFMPH on C-18 | 0.0717 | 0 | 175 | 175 | 0.0958 | 0.08375 | 14.65625 | 0.01465625 | 292 |
| SKC-9 | KI #2 | TFMPH on C-18 | 0.0424 | 0 | 175 | 175 | 0.0598 | 0.0511 | 8.9425 | 0.0089425 | 292 |
| | no KI #2 | TFMPH on C-18 | 0.0525 | 0 | 175 | 175 | 0.0695 | 0.061 | 10.675 | 0.010675 | 292 |
| Gillian-9907 | KI #3 | TFMPH on C-18 | 0.0491 | 0 | 175 | 175 | 0.0602 | 0.05465 | 9.56375 | 0.00956375 | 292 |
| | no KI #3 | TFMPH on C-18 | 0.0606 | 0 | 175 | 175 | 0.062 | 0.0613 | 10.7275 | 0.0107275 | 292 |

| Temp. Corr. Vol (m3) | Tot. Mass Coll'td (mcg) | Blank Corr. Mass (mcg) | Air [ ] (mcg/m3) | Air [ ] (ppm) |
|---|---|---|---|---|
| 0.098495634 | | 0.611 | 6.203320674 | 0.005059842 |
| 0.091173202 | | 0.814 | 8.928061993 | 0.007282323 |
| 0.015028844 | | 0.0331 | 2.202431512 | 0.00179645 |
| 0.014957406 | | 0.0216 | 1.444100685 | 0.001177905 |
| 0.00912625 | | none detect'd | #REF! | #REF! |
| 0.010894349 | | none detect'd | #REF! | #REF! |
| 0.009760265 | | 0.0679 | 6.956778032 | 0.005674412 |
| 0.010947928 | | 0.0501 | 4.576208359 | 0.003732661 |

**Sampling Location:** LM roof, Day 14, KI check, 11 am-9 pm
**Date:** May 18, 1999

| Pump # | Sample I.D. | Method | Initial F.R. (l/min) | Start (min) | End (min) | Sampling Time (min) | (l/min) Final F.R. | (l/min) Avg. F.R. | Sample Vol (l) | Sample Vol (m3) |
|---|---|---|---|---|---|---|---|---|---|---|
| Buck-2 | 11-2 pm | DNPH #1 | 0.841 | 0 | 180 | 180 | 0.842 | 0.8415 | 151.47 | 0.15147 |
| Buck-2 | 11-2 pm | DNPH #2 | 0.847 | 0 | 180 | 180 | 0.838 | 0.8425 | 151.65 | 0.15165 |
| SKC-95 | 11-2 pm | TFMPH KI #1 | 0.047 | 0 | 180 | 180 | 0.046 | 0.0465 | 8.37 | 0.00837 |
| Gillian9902 | 11-2 pm | TFMPH KI #2 | 0.064 | 0 | 180 | 180 | 0.06 | 0.062 | 11.16 | 0.01116 |
| SKC-95 | 11-2 pm | TFMPH no KI #1 | 0.051 | 0 | 180 | 180 | 0.05 | 0.0505 | 9.09 | 0.00909 |
| Gillian9902 | 11-2 pm | TFMPH no KI #2 | 0.06 | 0 | 180 | 180 | 0.058 | 0.059 | 10.62 | 0.01062 |
| Buck-4 | 2-5 pm | DNPH #1 | 1.073 | 0 | 180 | 180 | 1.039 | 1.056 | 190.08 | 0.19008 |
| SKC-44 | 2-5 pm | TFMPH KI #1 | 0.106 | 0 | 180 | 180 | 0.102 | 0.104 | 18.72 | 0.01872 |
| Gillian396 | 2-5 pm | TFMPH KI #2 | 0.069 | 0 | 180 | 180 | 0.067 | 0.068 | 12.24 | 0.01224 |
| SKC-44 | 2-5 pm | TFMPH no KI #1 | 0.109 | 0 | 180 | 180 | 0.103 | 0.106 | 19.08 | 0.01908 |
| Gillian396 | 2-5 pm | TFMPH no KI #2 | 0.073 | 0 | 180 | 180 | 0.071 | 0.072 | 12.96 | 0.01296 |
| Buck-2 | 5-9 pm | DNPH #1 | 0.725 | 0 | 240 | 240 | 0.731 | 0.728 | 174.72 | 0.17472 |
| Buck-2 | 5-9 pm | DNPH #2 | 0.963 | 0 | 240 | 240 | 0.976 | 0.9695 | 232.68 | 0.23268 |
| SKC-95 | 5-9 pm | TFMPH KI #2 | 0.05 | 0 | 240 | 240 | 0.043 | 0.0465 | 11.16 | 0.01116 |
| SKC-95 | 5-9 pm | TFMPH no KI #2 | 0.044 | 0 | 240 | 240 | 0.049 | 0.0465 | 11.16 | 0.01116 |

| Sampl. Temp (K) | Temp. Corr. Vol (m3) | Tot. Mass Coll'td (mcg) | Blank Corr. Mass (mcg) | Air [ ] (mcg/m3) | Air [ ] (ppm) |
|---|---|---|---|---|---|
| 293 | 0.154054812 | | 2.43 | 15.77360658 | 0.012866005 |
| 293 | 0.154237884 | | 1.98 | 12.83731305 | 0.010470968 |
| 293 | 0.008512833 | | 0.109 | 12.80419844 | 0.010443958 |
| 293 | 0.011350444 | | 0.284 | 25.02104833 | 0.020408835 |
| 293 | 0.009245119 | | 0.017 | 1.838808042 | 0.001499854 |
| 293 | 0.010801229 | | 0.459 | 42.49516551 | 0.03466189 |
| 293 | 0.193323686 | | 2.81 | 14.53520806 | 0.011855885 |
| 293 | 0.019039454 | | 0.117 | 6.145134228 | 0.005012381 |
| 293 | 0.012448874 | | 0.148 | 11.8886257 | 0.009697156 |
| 293 | 0.019405597 | | 0.036 | 1.855134861 | 0.001513172 |
| 293 | 0.01318116 | | 0.025 | 1.896646367 | 0.001547031 |
| 293 | 0.17770157 | | 2.72 | 15.30656145 | 0.012485052 |
| 293 | 0.236650648 | | 2.87 | 12.12758139 | 0.009892064 |
| 293 | 0.011350444 | | 0.197 | 17.35614972 | 0.014156833 |
| 293 | 0.011350444 | | 0.044 | 3.876500445 | 0.003161932 |