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### Low Molecular Weight Carbonyls in Large Midwestern Office Buildings

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## LOW MOLECULAR WEIGHT CARBONYLS IN LARGE MIDWESTERN OFFICE BUILDINGS

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Airborne carbonyls in large office buildings in the Midwestern United States have been studied both indoors and near the air-intakes environment using HPLC and GCMS methods. Air sampling for carbonyls was conducted using 2,4-dinitrophenylhydrazine coated silica gel cartridges and stainless steel Tenax TA<sup>®</sup> tubes. 1,3-dinitrobenzene, 2,4-dinitrophenol and 2,4-dinitroaniline were tentatively identified as degradation products of 2,4-dinitrophenylhydrazine by HPLC and GCMS analysis. Performance of the Tenax TA<sup>®</sup>-GCMS method under field sampling conditions was studied and Tenax TA<sup>®</sup> data was validated to estimate the lowest possible concentration of carbonyls in the environment, using a correction term derived from error propagation analysis. Analytical recovery, analytes' breakthrough percentage, and limitations of the DNPH-cartridge sampling are presented along with GCMS ion fragmentation data of the tentatively identified product(s). Carbonyls including formaldehyde ( $6.8 \pm 8.8$  ppbv),<sup>+</sup> acetaldehyde ( $2.8 \pm 3.2$  ppbv), acetone ( $4.7 \pm 8.9$  ppbv), methyl ethyl ketone ( $0.4 \pm 0.7$  ppbv), 4-methyl-2-pentanone ( $0.5 \pm 1.7$  ppbv), n-hexanal ( $0.2 \pm 0.6$  ppbv) and n-heptanal ( $0.2 \pm 1.8$  ppbv) were present in indoor air. Outdoor concentrations were: formaldehyde,  $2.1 \pm 3.1$  ppbv; acetaldehyde,  $2.2 \pm 2.4$  ppbv; acetone,  $1.4 \pm 3.1$  ppbv; methyl ethyl ketone,  $0.6 \pm 0.4$  ppbv; 4-methyl-2-pentanone,  $0.2 \pm 0.1$  ppbv; n-hexanal,  $0.2 \pm 0.5$  ppbv; and n-heptanal ( $0.2 \pm 0.4$  ppbv). Total carbonyl concentrations ( $\Sigma_{CO}$ ) were  $15.6 \pm 13.2$  ppbv and  $6.9 \pm 5.1$  ppbv in indoor and outdoor air respectively. Average formaldehyde levels (7ppbv) in non-complaint buildings were lower than the recommended concentration levels in indoors of residential environment (100 ppbv).

$$\text{ppbv} = \frac{(\text{ng} \cdot \text{L}^{-1}) \cdot 24.45}{(\text{molecular weight})}$$

**Keywords:** Environmental air quality; DNPH-HPLC; carbonyls; 2,4-dinitroaniline; 2,4-dinitrophenol; Tenax TA-thermal desorption-GCMS

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## INTRODUCTION

Development of regulatory air quality standards for rural and metropolitan areas of agricultural Midwestern United States requires an understanding of the various chemical species present in the particular environment and their physico-chemical characteristics including diffusive distribution and cross reactions with one another. In the rural environments, chemical constituents of both volatile and semi-volatile origin are very complex and arise partly from extensive application of fertilizers, pesticides and herbicides in agriculture, feed preservatives and animal farms. Environmental air quality in indoor environments including residences, schools and office buildings has become an increasingly significant concern to respiratory environmental health professionals evidenced by numerous incidences of sick building syndrome (SBS) [1–5].

The presence of myriad of volatile and semi-volatile chemicals in the indoor work environment results from the consumers' utilization of cleaning agents, disinfectants, synthetic air fresheners, cosmetics, and technologic appliances, etc. In sick buildings, one of the most prevalent groups of volatile organic compounds is carbonyls, and aliphatic aldehydes in particular. Carbonyls are a significant fraction of non-methane hydrocarbon compounds present in the environment [6, 7]. One major sources of non-methane aldehydes such as acetaldehyde ( $\text{CH}_3\text{CHO}$ ) and methyl ethyl ketone (MEK) in urban outdoor air are automobile exhausts and oxidation of hydrocarbons in the atmosphere [8]. Sources of formaldehyde (HCHO) and  $\text{CH}_3\text{CHO}$  in the rural environment include oxidation of natural, anthropogenic, and biogenic non-methane hydrocarbons [9].

HCHO, the lowest molecular weight C1-carbonyl, is released from synthetic carpets and fiber boards. Repeated heat cycling in the winter months increases concentrations of HCHO, especially in "energy-saving" buildings, which lack proper ventilation. Other sources of indoor HCHO are disinfectants containing HCHO-releasing biocidal preservatives and personal care products such as cosmetics and shampoos [10, 11]. HCHO is a skin and eye irritant, may cause skin sensitization and may degenerate the mucosal lining in the respiratory tract, liver and kidney at low concentrations [12]. Short-term exposure effects include dyspnea, CNS effects and difficulty in urination. Long term effects include contact dermatitis, occupational asthma and Hodgkin's disease. Physiologically, HCHO is very reactive towards deoxy ribonucleic acids and forms DNA-formyl adduct at guanine amino group ( $-\text{N}=\text{CH}_2$ ). Toxicological studies suggest HCHO is an animal carcinogen at high concentrations. An inhalation exposure to HCHO and regulatory concentrations in the occupational settings have been reviewed [13,14]. American Conference on Governmental Industrial Hygienists (ACGIH) ceiling value is 300 ppbv. National Institute of Occupational Safety and Health (NIOSH)

recommended exposure limit (REL) is 16 ppbv. Acetaldehyde ( $\text{CH}_3\text{CHO}$ ), a C2-carbonyl, is also released from synthetic fibers and latex paints [15].  $\text{CH}_3\text{CHO}$  is a lachrymator. Acetone, acrolein, MEK, 4-methyl-2-pentanone (MIBK) are used as solvents. MEK is an irritant and can cause narcosis. Hexanal and heptanal are used as ingredients in deodorants and also generated from the oxidative ozonolysis of unsaturated hydrocarbons [16]. Exposure to the above aldehydes will increase glutathione peroxidase activity and reduce glutathione S-transferase and glutathione reductase activities [12]. In the atmospheric environment, trace levels of ozone and its products with aldehydes and  $\text{HNO}_3$  will generate hydroperoxides, peroxides and peroxyalkylnitrites (PAN) in ambient air [17, 18].

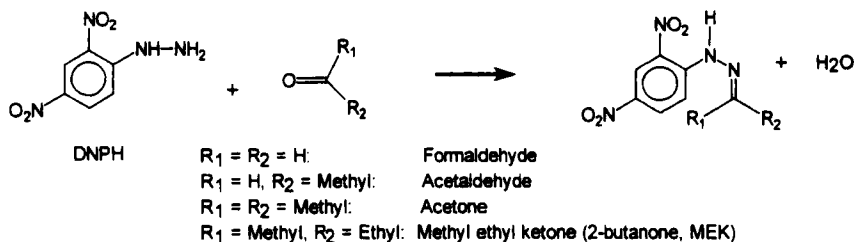
### Carbonyls in non-complaint office buildings

We have investigated the presence and distribution of low molecular weight carbonyls and indoor air quality related health symptoms in large office buildings in 'non complaint environments'. Our environmental air quality study was specifically designed to measure physical and chemical determinants and psychosocial attributes of workers in large office buildings to characterize the baseline information in non-complaint office buildings. Our study has primarily focused in six private buildings from the States of Iowa, Nebraska and Minnesota of the Mid-western USA. We collected basic data on indoor and outdoor environmental quality determinants (EQD) including temperature, volatile chemicals generation and distribution, humidity, ventilation/air exchange, lighting arrangements, microbial count, particulate and psychosocial attributes of the employees. Database containing these parameters has been developed by the United States Environmental Protection Agency (US-EPA). Large EQD-database will allow future identification and characterization of cross sectional and longitudinal variations of the environmental air quality determinants, interrelationships among indoor air quality and human exposures, and building design and operation. The two years study from November 1996 to October 1998 has covered all four seasons.

### Ambient air sampling for carbonyls

Several sampling media and analytical methods are available for sampling and analysis of volatile carbonyl compounds present in the air. Sodium bisulfite has been used in the impinger solutions [19] and cellulose fiber filters [20]. Solid adsorbent such as Chromosorb or XAD-2 resin coated with 2-benzylaminoethanol has been used for the collection of airborne aldehydes, followed by extraction

of 'benzyloxazolidines' in carbon disulfide and GC-FID analysis [21]. Matthews and his coworkers collected HCHO on 13X molecular sieve, desorbed in deionized water and analyzed by a photometric-'pararosaniline' method [22]. Recent sampling methods include the use of 2,4-dinitrophenylhydrazine (DNPH) as an absorbent media. DNPH-reagent has been used as an acetonitrile solution in impingers [23], coated as an impregnated surface-reagent on glass fiber filter paper [24], XAD-2 resin [25], Chromosorb P [26], Sep pak C-18 [27] and silica gel [28-31]. Carbonyl functional groups ( $>C=O$ ) from airborne aldehydes and ketones undergo Schiff's base condensation with DNPH to their respective hydrazone adducts ( $>C=N-$ ) in mild acidic conditions as shown below. DNPH-adducts are generally analyzed by reverse phase HPLC-UV method because these hydrazones possess high molar extinction coefficient ( $1.5$  to  $3.0 \times 10^4$ ) at 360 nm. DNPH adducts are also analyzed by HPLC-EC detection [32] and GCMS analysis [33].



Airborne volatile organic compounds such as carbonyls, alcohols, esters, aliphatics, aromatics and halocarbons have been collected on Tenax [34,35] and Carbosieve adsorbents [36,37], and analyzed by thermal desorption and GCMS. Summa canister methods are not suitable for the quantitation of polar organic compounds including carbonyls and alcohols though this method offers simplicity in the field sampling and analysis. In addition, a rigorous quality assurance and quality control (QA/QC) is required towards method validation due to lack of complete understanding on the degradation of target analytes by humidity and canister-surface catalytic reactions [55].

We collected volatile organic compounds including carbonyls that were present in the air, both indoor and outdoor close to the air-intake sources. Air samples were collected using DNPH coated silica gel cartridges and Tenax TA<sup>®</sup> tubes. Following sampling, target analytes from these two media were quantitated by RP-HPLC and TD-GCMS techniques, respectively. Field data including the identification and distribution of various carbonyls from these large office buildings is presented in this report. Analytical parameters such as extraction recovery, analytes' breakthrough under field sampling conditions and limitations of the sampling are also summarized.

## EXPERIMENTAL

### Reagents

Deionized water (18m $\Omega$ ) was collected from a NANO pure water system (Barnstead Thermolyne, Inc. IA). HPLC grade water (Optima) and o-phosphoric acid were purchased from Fisher Scientific Company (Chicago, IL). HPLC grade CH<sub>3</sub>CN was received from Aldrich (Milwaukee, WI). DNPH, 2,4-dinitroaniline (DNA), 2,4-dinitrophenol (DNP), CH<sub>3</sub>CHO, MEK, 4-methyl-2-pentanone (methyl isobutyl ketone, MIBK), n-hexanal, 2-hexanone, n-heptanal and 2-ethyl-hexanal were obtained from Aldrich Chemicals (Milwaukee, WI). HCHO was from Merck EM (St. Louis, MO). DNPH coated silica gel cartridges (1000  $\mu$ g or 500  $\mu$ g DNPH, 350 mg silica gel per cartridge, 200 – 250  $\mu$ m particle and 60/100 mesh size) and potassium iodide cartridges were obtained from Supelco (Bellefonte, PA) and used as received. Stainless steel Tenax TA<sup>®</sup> tubes were custom prepared (Supelco, Bellefonte, PA). Calibration standards containing HCHO, CH<sub>3</sub>CHO and acetone adducts of DNPH were prepared in house or custom made in an independent laboratory (Supelco, Bellefonte, PA). Bromochloromethane, 1,4-difluorobenzene, d5-chlorobenzene, 1,2-dichloroethane, d8-toluene, and bromofluorobenzene were obtained from Restek Corporation (Bellefonte, PA). Air sampling pumps and calibration devices were purchased from SKC Inc. (Eighty Four, PA).

### Methods

#### *Sampling design*

Air samples for aldehydes and ketones were collected in large buildings from the States of Iowa, Nebraska and Minnesota of Midwestern USA. Building description and number of occupants in the sampling areas are presented in Table I. In general, samples were collected from 4 different locations (3 locations in indoor and 1 in outdoor). One 'in-series' sampling was carried out in the indoor environment to determine 'breakthrough estimates' of target analytes through the sampling cartridges under field conditions. Duplicate sampling also was carried out at one indoor and one outdoor location (parallel sampling) to evaluate the reproducibility of the sampling and analysis.

#### *Air sampling*

An 8-hour time integrated sampling was carried out at the level of workers' breathing zone (ca. 1.1  $\pm$  0.3 m) during the daytime, between 08.00 to

18.00 hours. Sampling pumps were operated at  $0.2 \pm 0.02 \text{ L}\cdot\text{min}^{-1}$  for DNPH-cartridges and  $0.05 \pm 0.005 \text{ L}\cdot\text{min}^{-1}$  for Tenax TA<sup>®</sup> tubes, unless otherwise indicated. Total sample volumes were calculated from arithmetic mean flow rates measured from the calibration of the pumps prior to sampling and after sampling events. The target air volumes were in the range 96 L and 25 L for DNPH-coated silica gel cartridges and Tenax TA<sup>®</sup> tubes respectively. Potassium iodide cartridges were used as an ozone scavenger in selected sampling sites. Each sampling-trip included 2 blind QA/QC samples, 3 trip blanks and 3 laboratory blanks. Sampling cartridges were stored in aluminum-cans filled with an activated charcoal and transported at 4°C.

TABLE I Large office buildings' description for the field sampling of carbonyls in the States of Iowa, Nebraska and Minnesota of Midwestern USA

<i>Building Description</i>	<i>Sampling location</i>	<i>Estimated number of occupants (indoor sampling area, m<sup>2</sup>)</i>	<i>Seasons sampled</i>
DM1-IA	3rd and 4th floors in a 4-story building	210 (5930)	Fall, winter, spring and summer
DM2-IA	4th floor in a 15-story building	55 (1370)	Fall, winter and spring
OM1-NE	8th, 9th and 13th floors in a 17-story building	201 (6130)	Fall, winter, spring and summer
SP1-MN	8th floor in an Inter connected 14-story building	59 (2150)	Fall, winter, spring and summer
MI1-MN	5th and 7th floors in a 10-story building	78 (2810)	Fall, winter, spring and summer
PL1-MN	2nd floor in a 4-story building	66 (3150)	Fall, winter, spring and summer

## Analysis of air samples

### HPLC

Following sampling, DNPH cartridges (blanks, blind QA/QC standards and samples) were extracted and analyzed within 14 days. DNPH cartridges were extracted into volumetric flasks (5.0 mL) using CH<sub>3</sub>CN as an eluent and analyzed immediately. Analyses were carried out using a HPLC system equipped with a guard column (Supelco, 2 × 0.4 cm), spherical-ODS RP-C18 analytical column (Supelco, LC-18, 5µm particle, 100 Å pore, 15 × 0.46 cm), UV-VIS detector (Dionex) and HPLC gradient system (Dionex). HPLC analyses of PNA, DNA and DNPH-adducts were monitored at 360 nm. An aliquot of the test mix-

ture was manually injected using a Rheodyne 7020 injector (Rheodyne, CA). The injection volume was 20  $\mu\text{L}$  (fixed loop). Chromatographic separation was accomplished under an isocratic conditions using 60%  $\text{CH}_3\text{CN}$  as an eluent at a flow rate of 1.0  $\text{mL}\cdot\text{min}^{-1}$  [28]. Concentration of  $\text{HCHO}$ ,  $\text{CH}_3\text{CHO}$  and acetone in the extracts were determined from a five point linear calibration using a standard mixture containing DNPH- $\text{HCHO}$ , DNPH- $\text{CH}_3\text{CHO}$  and DNPH-acetone adducts. Calibration lines of hydrazone adducts were linear for the concentration range 10  $\mu\text{g}\cdot\text{L}^{-1}$  to 2000  $\mu\text{g}\cdot\text{L}^{-1}$ .

### ***GCMS of DNPH-extracts***

Acetonitrile extracts from the sampling cartridges and synthetic DNPH-adducts were analyzed by GCMS using 2  $\mu\text{L}$  injections. Positive ion mass spectrometric analysis was carried out using HP-5970B MSD mass spectrometer and DB-5 column (30 meters, 0.25 mm i.d., and 0.5  $\mu\text{m}$  film thickness). Gas chromatographic conditions for positive ion analysis were: solvent delay time = 2.0 minutes; initial temperature = 60°C; initial time = 1 minute; temperature gradient = 10°C $\cdot\text{min}^{-1}$ ; final temperature = 300°C and final time = 7 minutes. Negative ion mass spectrometric analysis was carried out using Finnigan Mat GCQ mass spectrometer and DB-1 column (15 meters, 0.32 mm i.d., and 1.0  $\mu\text{m}$  film thickness) for a blank and three field samples that were preserved for 22 months at -20°C. Methane was used as collision gas. Filament voltage was 70 eV. Gas chromatographic conditions for negative ion analysis were: solvent delay time = 2.5 minutes; initial temperature = 80°C; temperature gradient = 20°C $\cdot\text{min}^{-1}$ ; final temperature = 280°C and final time = 20 minutes.

### ***Thermal desorption-GCMS***

Tenax TA<sup>®</sup> (1.5 g) in stainless steel tubes (11.5  $\times$  0.6 cm) was conditioned by thermal desorption at 270°C for 50 minutes at a flow rate of 0.06  $\text{L}\cdot\text{min}^{-1}$  using helium carrier gas. Samples were initially desorbed at 270°C (0.04  $\text{L}\cdot\text{min}^{-1}$ , 5 minutes) to Tenax trap (-40°C) followed by rapid desorption at 220°C to cryofocusser (-150°C). The sample mixture was then injected onto DB-1 GC column (30 meters, 0.25 mm i.d., and 1.0  $\mu\text{m}$  film thickness) for up to five minutes by rapid heating of the cryofocusser to 120°C. GC conditions were: solvent delay time = 2.0 minutes; initial temperature = 35°C, initial time = 2 minutes; temperature gradient 1 = 4°C  $\text{mL}\cdot\text{min}^{-1}$  to 60°C; holding time 1 = 0 minute; temperature gradient 2 = 8°C  $\text{mL}\cdot\text{min}^{-1}$  to 150°C; holding time 2 = 0 minutes; temperature gradient 3 = 25°C  $\text{mL}\cdot\text{min}^{-1}$  to 270°C and final time 3 = 12 minutes. Mass spectral data was collected on electron impact/positive ion mode using HP-5972A MSD mass spectrometer. 5 point calibration was established for the target com-



pounds using the quantitation ions  $m/z = 43, 72, 43, 43, 44, 41$  and  $72$  for acetone, MEK, MIBK, 2-hexanone, n-hexanal, n-heptanal and 2-ethylhexanal respectively. Calibration curves were nonlinear in the analytical range  $10$  ng to  $100$  ng per cartridge. Carbonyls concentrations by GCMS were estimated using average response factors of target analytes ( $10$  ng to  $100$  ng load) which in turn were corrected against internal standards. Bromochloromethane ( $m/z = 128$ ), 1,4-difluorobenzene ( $m/z = 114$ ), d5-chlorobenzene ( $m/z = 117$ ) were used as internal standards. 1,2-dichloroethane ( $m/z = 65$ ), d8-toluene ( $m/z = 98$ ), and bromofluorobenzene ( $m/z = 75$ ) served as surrogate standards.

## RESULTS

### HPLC

HPLC analysis of blanks and field samples indicated the presence of large excess of unreacted DNPH. Field samples contained  $99 \pm 8\%$  of the original DNPH-reagent ( $n = 54$  and  $1000\text{ }\mu\text{g}$  per cartridge). All the errors are reported as 1 standard deviation ( $\pm 1\sigma$ ).  $91 \pm 4\%$  of the original DNPH-reagent was estimated from cartridges containing  $500\text{ }\mu\text{g}$  of DNPH ( $n = 78$ ). All silica gel cartridges contained HCHO,  $\text{CH}_3\text{CHO}$  and acetone as background in blank cartridges. The lowest HCHO concentrations were  $35$  ng per cartridge and  $16$  ng per cartridge for  $1000\text{ }\mu\text{g}$  and  $500\text{ }\mu\text{g}$  DNPH-reagent respectively.  $1000\text{ }\mu\text{g}$  DNPH coated blank-cartridges had  $55 \pm 28$  ng HCHO,  $90 \pm 64$  ng  $\text{CH}_3\text{CHO}$  and  $226 \pm 163$  ng acetone ( $n = 69$ ).  $500\text{ }\mu\text{g}$  DNPH coated blank cartridges had  $33 \pm 29$  ng HCHO,  $56 \pm 36$  ng  $\text{CH}_3\text{CHO}$  and  $208 \pm 97$  ng acetone ( $n = 78$ ). Practical quantitation limits ( $12\sigma$ ) were calculated from 7 spiked DNPH-cartridges ( $100$ – $150$  ng). Analytes' recovery percentage was also estimated for HCHO,  $\text{CH}_3\text{CHO}$  and acetone from 48 of total 52 blind DNPH cartridge samples having concentrations in the range  $100$  ng to  $5000$  ng. Breakthrough percentage of HCHO,  $\text{CH}_3\text{CHO}$  and acetone was calculated from 23 sampling events. Method performance data including practical quantitation limits, blind QA/QC-samples' recovery and breakthrough percentage values are summarized in Table II.

HPLC analysis of field samples indicated the presence of three major carbonyls. HCHO,  $\text{CH}_3\text{CHO}$ , and acetone were tentatively identified as DNPH-hydrazones (**1**, **2** and **3**) and had retention times ( $t_r$ )  $4.0 \pm 0.1$  min.,  $5.0 \pm 0.1$  min., and  $6.2 \pm 0.2$  min. respectively. Seasonal distribution of airborne concentration data of HCHO,  $\text{CH}_3\text{CHO}$  and acetone in indoor and outdoor of all six buildings is presented in Table III.

TABLE II Analytical methods performance data: practical quantitation limits (12  $\sigma$ ), blind spike recovery and field breakthrough percentage through the sampling media

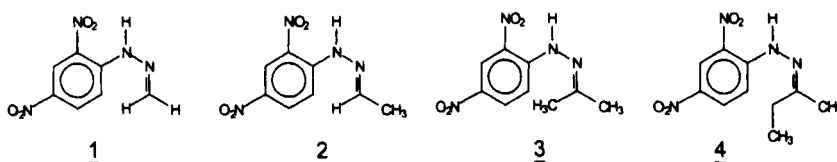
Analyte	DNPH – HPLC			Tenax – GCMS		
	Mean recovery % (warning limit %, 2σ)	PQL (12σ) (ppbv)	Field break-through %	PQL (12σ) (ppbv)	Laboratory breakthrough ± 1σ %	Field breakthrough %
Formaldehyde	107 (87 – 127)	1.5	2	–	–	–
Acetaldehyde	105 (89–121)	3.5	6	–	–	–
Acetone	100 (62 – 137)	9.0	7	0.1	40 ± 30	50
2-Butanone (MEK)	–	–	–	0.1	50 ± 40	50
4-Methyl-2-pentanone	–	–	–	0.1	< 5	40
2-Hexanone	–	–	–	0.1	< 5	–
n-Hexanal	–	–	–	0.1	< 5	40
n-Heptanal	–	–	–	0.1	< 5	60
2-Ethylhexanal	–	–	–	0.1	< 5	–

TABLE III Indoor and outdoor concentration data ( $\mu\text{g m}^{-3}$ ) of HCHO,  $\text{CH}_3\text{CHO}$  and acetone from six buildings estimated by DNPH-cartridge sampling and HPLC analysis

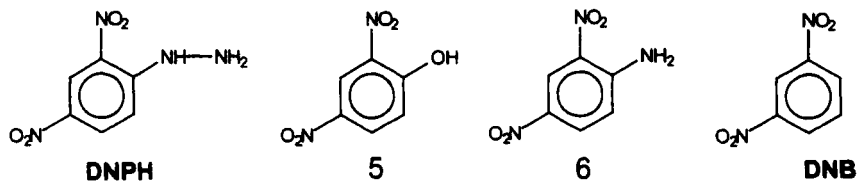
Building-Location	Fall (mean $\pm$ 1 std dev.)		Winter (mean $\pm$ 1 std dev.)		Spring (mean $\pm$ 1 std dev.)		Summer (mean $\pm$ 1 std dev.)	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
<b>DM1 – IA</b>								
Formaldehyde	6.2 $\pm$ 0.9	4.1 $\pm$ 3.7	13.7 $\pm$ 3.6	1.9 $\pm$ 0.4	9.2 $\pm$ 1.2	0.8 $\pm$ 0.6	19.3 $\pm$ 1.8	1.7 $\pm$ 0.4
Acetaldehyde	2.5 $\pm$ 0.2	1.7 $\pm$ 0.1	7.7 $\pm$ 2.1	63 $\pm$ 0.6	5.4 $\pm$ 0.8	3.4 $\pm$ 1.8	6.7 $\pm$ 10.6	4.7 $\pm$ 0.6
Acetone	20.7 $\pm$ 23.2	11.9 $\pm$ 11.4	15.7 $\pm$ 3.9	2.7 $\pm$ 0.3	12.1 $\pm$ 3.1	No data	23.5 $\pm$ 4.0	5.5 $\pm$ 2.8
<b>DM2 – IA</b>								
Formaldehyde	2.2 $\pm$ 0.5	0.8 $\pm$ 0.2	6.7 $\pm$ 1.3	1.8 $\pm$ 0.2	6.5 $\pm$ 0.5	3.2 $\pm$ 0.1	No data	No data
Acetaldehyde	0.6 $\pm$ 0.3	0.6 $\pm$ 0.1	4.0 $\pm$ 1.7	1.7 $\pm$ 0.2	3.2 $\pm$ 0.2	2.8 $\pm$ 0.5	No data	No data
Acetone	1.7 $\pm$ 0.5	No Data	13.3 $\pm$ 3.9	2.2 $\pm$ 0.1	12.6 $\pm$ 1.3	4.7 $\pm$ 3.5	No data	No data
<b>OM1 – NE</b>								
Formaldehyde	8.4 $\pm$ 2.7	3.6 $\pm$ 0.2	8.2 $\pm$ 5.4	6.2 $\pm$ 2.7	6.6 $\pm$ 0.9	2.2 $\pm$ 0.1	12.4 $\pm$ 1.8	3.2 $\pm$ 1.4
Acetaldehyde	6.7 $\pm$ 1.2	6.8 $\pm$ 0.4	6.0 $\pm$ 2.3	8.0 $\pm$ 2.0	4.4 $\pm$ 0.2	7.7 $\pm$ 0.1	11.0 $\pm$ 1.4	6.2 $\pm$ 1.2
Acetone	14.0 $\pm$ 4.7	5.1 $\pm$ 0.7	0.6 $\pm$ 1.3	No data	5.8 $\pm$ 1.3	3.1 $\pm$ 0.1	36.8 $\pm$ 34.3	1.1 $\pm$ 1.6

<i>Building-Location</i>	<i>Fall (mean <math>\pm</math> 1 std dev.)</i>	<i>Winter (mean <math>\pm</math> 1 std dev.)</i>	<i>Spring (mean <math>\pm</math> 1 std dev.)</i>	<i>Summer (mean <math>\pm</math> 1 std dev.)</i>
<b>SP1 - MN</b>				
Formaldehyde	4.2 $\pm$ 0.4	4.8 $\pm$ 1.8	5.5 $\pm$ 0.4	5.2 $\pm$ 0.8
Acetaldehyde	2.5 $\pm$ 0.3	4.1 $\pm$ 1.5	4.0 $\pm$ 0.5	2.3 $\pm$ 0.3
Acetone	3.8 $\pm$ 0.7	3.6 $\pm$ 7.1	6.6 $\pm$ 0.7	5.6 $\pm$ 3.2
<b>MI1 - MN</b>				
Formaldehyde	12.4 $\pm$ 0.6	7.2 $\pm$ 0.2	8.9 $\pm$ 2.3	19.7 $\pm$ 2.3
Acetaldehyde	5.4 $\pm$ 0.5	3.9 $\pm$ 0.4	5.9 $\pm$ 0.2	10.2 $\pm$ 0.9
Acetone	12.4 $\pm$ 0.8	5.8 $\pm$ 0.5	18.5 $\pm$ 2.9	14.2 $\pm$ 1.6
<b>PL1 - MN</b>				
Formaldehyde	4.6 $\pm$ 0.7	4.9 $\pm$ 0.1	3.0 $\pm$ 0.5	12.0 $\pm$ 1.6
Acetaldehyde	2.9 $\pm$ 0.4	3.8 $\pm$ 0.4	3.6 $\pm$ 0.6	6.1 $\pm$ 0.9
Acetone	6.0 $\pm$ 0.4	5.1 $\pm$ 0.6	12.6 $\pm$ 4.0	13.7 $\pm$ 2.7

HPLC did not indicate the presence of acrolein and was further supported by GCMS studies. MEK was tentatively identified from field samples (**4**,  $t_r = 9.2 \pm 0.2$  min.). HPLC of synthetic DNPH-MEK adduct yielded both *E*- (25%) and *Z*- (75%) isomers (Figure 2, inset). Field samples that were tentatively identified to contain MEK had DNPH derivative as *Z*-isomer in the HPLC analysis (Figure 2). MEK was identified in indoors of all six buildings (64% of 92 indoor samples). However, two indoor samples had a frontal broad-shoulder in the HPLC and possibly originated from *E*-isomer. All the outdoor samples ( $n = 46$ ) contained MEK. HPLC analysis did not provide *E*-isomer for the synthetic DNPH-  $\text{CH}_3\text{CHO}$  adduct (*vide infra*).



HPLC analysis of field samples indicated the presence of 2,4-dinitrophenol (**5**) and 2,4-dinitroaniline (**6**). **5** had the chromatographic retention time ( $t_r = 1.4$  min.). **6** co-eluted or as a shoulder peak ( $t_r = 3.1$  min.), immediately next to the DNPH-reagent peak ( $t_r = 2.9$  min.). **5** and **6** were tentatively identified from the HPLC analysis of authentic standards and confirmed by the GCMS analysis (*vide infra*). A representative HPLC of a field blank (trace 1A) and an 'in-series' field samples (trace 1B and 1C) are reconstructed in Figure 1. Comparative chromatographic traces obtained for a typical indoor (trace 2A) and an outdoor (trace 2B) sample from the same sampling event is presented in Figure 2.



An unambiguous identification of the product eluted under the chromatographic peak **X** was not successful. However, relative-yield distribution ratio for **X** and **1** was estimated with the assumption that **X** and **1** had similar molecular weights and molar extinction coefficients. Chromatographic peak area of **X** and **1** indicated these two compounds were present in the ratio  $1: 5.6 \pm 3.3$  in indoor

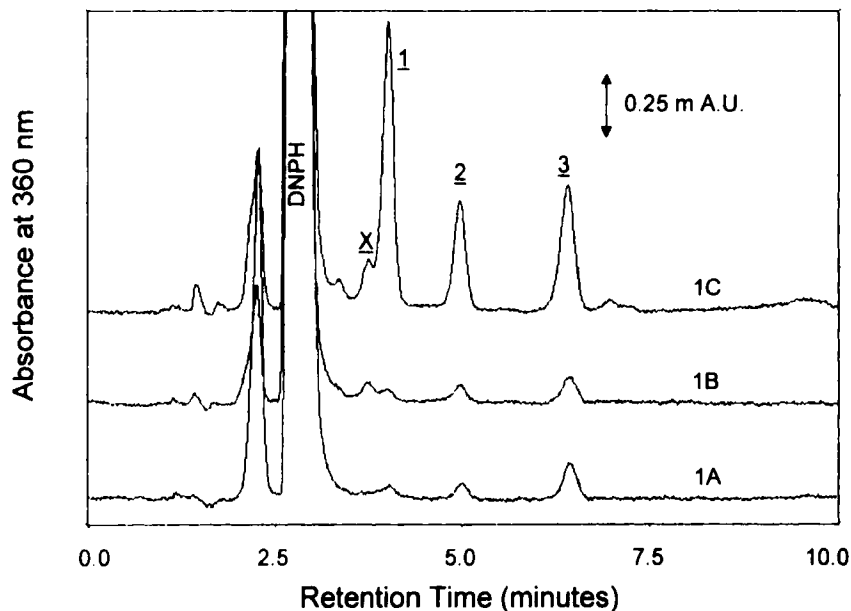


FIGURE 1 A representative HPLC of the carbonyl-hydrazones collected on to DNPH cartridges from a single sampling event. Trace 1A: field blank. Trace 1B and 1C: Two sampling cartridges were connected 'in-series'. Trace 1C, first cartridge in the series, and air was only allowed to enter through it. Trace 1B, second cartridge in the series and it was connected to the first cartridge, as a backup

samples ( $n = 48$ ) and 1:  $2.2 \pm 2.1$  ratio in outdoor samples ( $n = 38$ ). The use of potassium iodide cartridge did not reduce the peak intensity for the product **X** significantly. Peak intensity change was  $21.6 \pm 10.2\%$  ( $n = 2$  from 3 trials) in indoor environmental samples. The peak intensity of **X** had reduced by 76.3% ( $n = 1$  from 3 trials) for an outdoor sample with reference to a control sample.

### GCMS of DNPH-extracts

Acetonitrile extract of a laboratory blank and a field sample was analyzed by GCMS. A representative total ion chromatogram (TIC) from an electron impact-positive ion analysis is reconstructed in Figure 3. DNPH-reagent eluted at  $t_R = 20.8$  min. ( $m/z = 198$  (32%),  $[M]^{+*}$ ; 182 (1%),  $[M-O]^{+*}$ ; 152 (2%),  $[M-NO_2]^{+*}$ ; 122 (24%),  $[M-NO-NO_2]^{+*}$ ; and 51 (100%). 1,3-dinitrobenzene (DNB) was present both in the blank and field sample ( $t_R = 12.5$  min.:  $m/z = 168$  (94%),  $[M]^{+*}$ ; 138 (5%),  $[M-NO]^{+*}$ ; 122 (31%),  $[M-NO_2]^{+*}$ ; 92 (57%),  $[M-NO-NO_2]^{+*}$ ; and 76 (92%),  $[M-(NO_2)_2]^{+*}$ ). DNA, DNPH-HCHO,

DNPH-CH<sub>3</sub>CHO and DNPH-acetone were eluted under the chromatographic peaks at 17.9 min., 18.0 min., 18.1 min. and 20.1 min. respectively (Figure 3). However, these products were not fully characterized from the field samples, mainly due to lack of sample concentration and sufficient ion-intensity for molecular ions and their fragmentation ions.

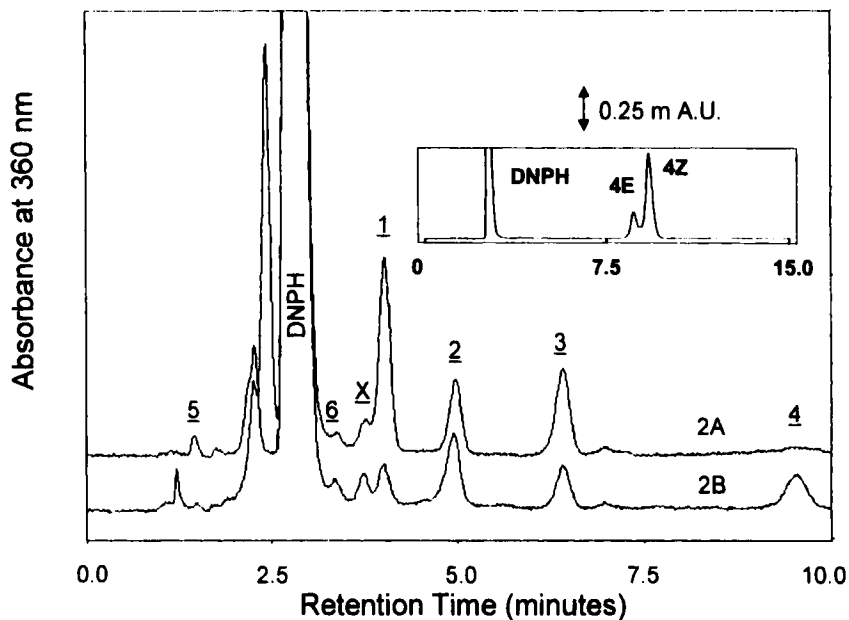


FIGURE 2 Comparative HPLC of the carbonyl-hydrazone in a typical indoor (trace 2A) and an outdoor (trace 2B) samples from the same sampling event. The inset is a HPLC of authentic DNPH-MEK derivative (E and Z isomers) with DNPH is shown as reference

Negative ion GCMS provided  $m/z = 182$  ( $[M-(N=CR_1R_2)]^-$  ion) as the base peak for all DNPH-carbonyl adducts and DNPH-reagent. Negative ion GCMS analysis of DNPH-hydrazone provided both E- and Z-isomers for CH<sub>3</sub>CHO and MEK (*vide supra*). DNPH-adducts were identified from negative ion GCMS (Figure 4): DNPH-HCHO ( $t_r = 5.4$  min.:  $m/z = 210$  (0.2%),  $[M]^-$ ; 194 (0.5%),  $[M-O]^-$ ; 193 (0.4%),  $[M-OH]^-$ ; 182 (100%),  $[M-(N=CH_2)]^-$ ; 166 (3.3%),  $[M-(O)-(N=CH_2)]^-$ ). DNPH-CH<sub>3</sub>CHO (**2E**,  $t_r = 6.1$  min.:  $m/z = 224$  (4.8%),  $[M]^-$ ; 208 (1.2%),  $[M-O]^-$ ; 207 (1.4%),  $[M-OH]^-$ ; 182 (100%),  $[M-(N=C(H)CH_3)]^-$ ; 166 (2.7%),  $[M-(O)-(N=C(H)CH_3)]^-$ ; 152 (1.9%),  $[M-(NO)-(N=C(H)CH_3)]^-$ ; and **2Z**,  $t_R = 6.2$  min.:  $m/z = 224$  (0.6%),  $[M]^-$ ; 208 (0.2%),  $[M-O]^-$ ; 207 (0.1%),  $[M-OH]^-$ ; 182 (100%),  $[M-(N=C(H)CH_3)]^-$ ; 166 (1.3%),  $[M-(O)-(N=C(H)CH_3)]^-$ ; 152 (1.0%),  $[M-(NO)-(N=C(H)CH_3)]^-$ ).

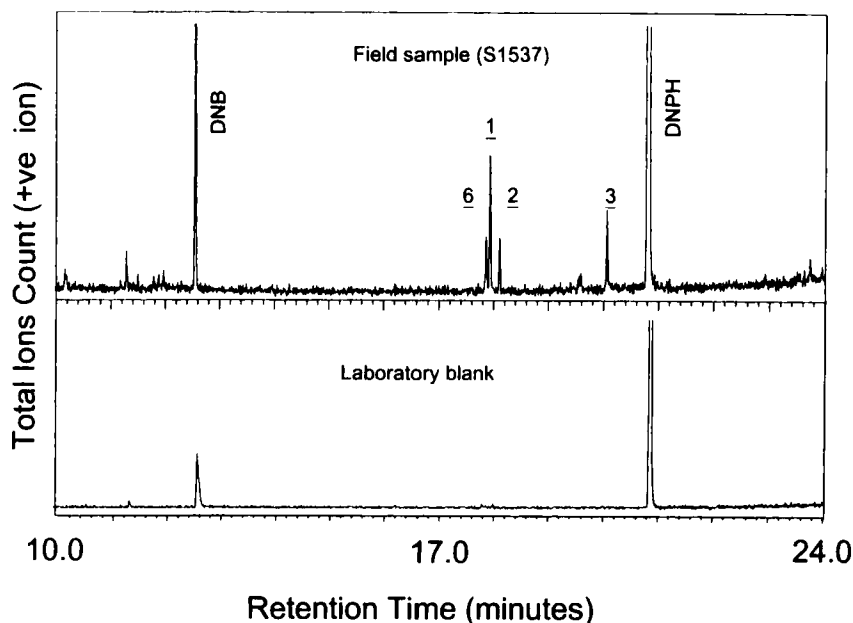


FIGURE 3 Total ion chromatogram (positive ion GCMS analysis) of  $\text{CH}_3\text{CN}$  extracts of DNPH-products from a blank (lower trace) and a field sample – AS1537 (upper trace)

DNPH-acetone ( $t_r = 6.4$  min.:  $m/z = 238$  (18.3%),  $[\text{M}]^-$ ; 222 (0.9%),  $[\text{M}-\text{O}]^-$ ; 221 (3.3%),  $[\text{M}-\text{OH}]^-$ ; 182 (100%),  $[\text{M}-(\text{N}=\text{C}(\text{CH}_3)_2)]^-$ ; 166 (1.8%),  $[\text{M}-(\text{O})-(\text{N}=\text{C}(\text{CH}_3)_2)]^-$ ; 152 (2.2%),  $[\text{M}-(\text{NO})-(\text{N}=\text{C}(\text{CH}_3)_2)]^-$ . DNPH-MEK (**4E**,  $t_r = 7.1$  min.:  $m/z = 252$  (31.6%),  $[\text{M}]^-$ ; 236 (1.4%),  $[\text{M}-\text{O}]^-$ ; 235 (4.1%),  $[\text{M}-\text{OH}]^-$ ; 182 (100%),  $[\text{M}-(\text{N}=\text{C}(\text{C}_2\text{H}_5)\text{CH}_3)]^-$ ; 166 (1.9%),  $[\text{M}-(\text{O})-(\text{N}=\text{C}(\text{C}_2\text{H}_5)\text{CH}_3)]^-$ ; 152 (1.6%),  $[\text{M}-(\text{NO})-(\text{N}=\text{C}(\text{C}_2\text{H}_5)\text{CH}_3)]^-$ ; and **4Z**,  $t_r = 7.2$  min.:  $m/z = 252$  (33.3%),  $[\text{M}]^-$ ; 236 (0.8%),  $[\text{M}-\text{O}]^-$ ; 235 (2.7%),  $[\text{M}-\text{OH}]^-$ ; 182 (100%),  $[\text{M}-(\text{N}=\text{C}(\text{C}_2\text{H}_5)\text{CH}_3)]^-$ ; 166 (1.2%),  $[\text{M}-(\text{O})-(\text{N}=\text{C}(\text{C}_2\text{H}_5)\text{CH}_3)]^-$ ; 152 (1.2%),  $[\text{M}-(\text{NO})-(\text{N}=\text{C}(\text{C}_2\text{H}_5)\text{CH}_3)]^-$ . Also, negative ion GCMS of field samples allowed the identification of DNB ( $t_r = 2.6$  min.:  $m/z = 168$  (100%),  $[\text{M}]^-$ ; 152 (4.0%),  $[\text{M}-\text{O}]^-$ ; 138 (84.9%),  $[\text{M}-\text{NO}]^-$ ; 122 (1.2%),  $[\text{M}-\text{NO}_2]^-$  and 46 (32.7%),  $[\text{NO}_2]^-$ ), **5** ( $t_R = 3.1$  min.:  $m/z = 184$  (1.7%),  $[\text{M}]^-$ ; 167 (100%),  $[\text{M}-\text{OH}]^-$ ; 154 (6.1%),  $[\text{M}-\text{NO}]^-$ ; 138 (3.3%),  $[\text{M}-\text{NO}_2]^-$ ; and 137 (7.9%),  $\text{M}-(\text{HNO}_2)]^-$ ) and **6** ( $t_r = 5.3$  min.:  $m/z = 183$  (29.4%),  $[\text{M}]^-$ ; 166 (100%),  $[\text{M}-\text{OH}]^-$ ; 153 (13%),  $[\text{M}-\text{NO}]^-$ ; 137 (3.4%),  $[\text{M}-\text{NO}_2]^-$ ; and 136 (6.2%),  $\text{M}-(\text{HNO}_2)]^-$ ). Reaction of sodium nitrite with DNPH-reagent gave two chromatographic peaks: DNB ( $t_r = 2.6$  min.) and 2,4-dinitrophenylazide (**7**,  $t_R = 3.3$  min.:  $m/z = 181$  (100%),  $[\text{M}-\text{N}_2]^-$ ; 167 (30.4%),  $[\text{M}-\text{N}_3]^-$ ; 166 (28.0%),



$[M-(H)-(N_3)]^-$ ; 165 (17.7%),  $[M-(O)-(N_2)]^-$ ; 163 (5.9%),  $[M-NO_2]^-$ ; 151 (6.3),  $[M-NO-(N_2)]^-$ ; and 46 (10%),  $[NO_2]^-$ .

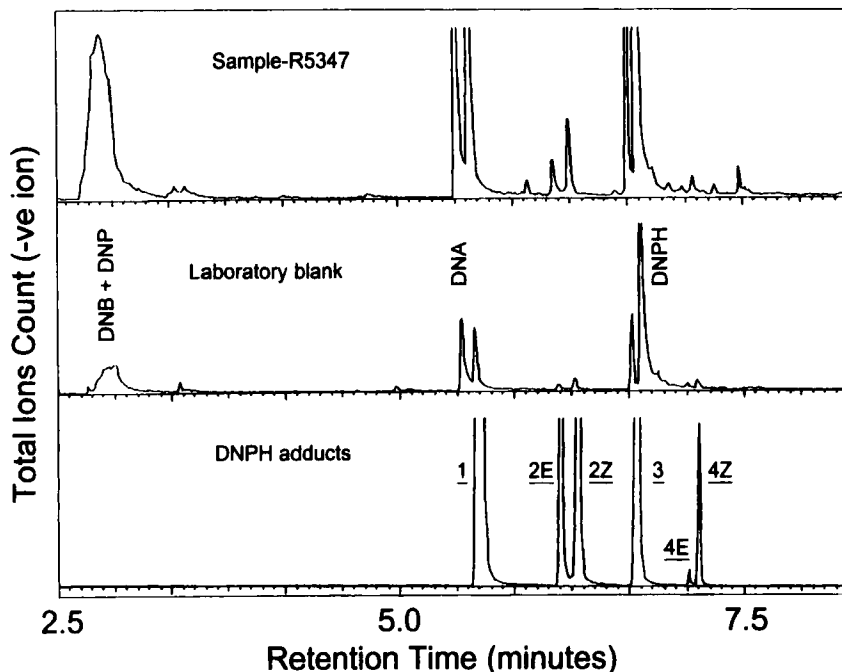


FIGURE 4 Total ion chromatogram (negative ion GCMS analysis) of  $CH_3CN$  extracts of DNPH-products from a field sample – R5347 (upper trace), a blank (middle trace) and authentic DNPH-hydrazone adducts (lower trace)

### Tenax TA-GCMS

Tenax TA sampling and thermal desorption-cryofocus GCMS analysis confirmed the presence of acetone, MEK, MIBK, 2-hexanone, n-hexanal and n-heptanal in the indoor environment. 2-ethylhexanal was not identified from field samples. In a few samples nonanal was identified as present by WILS-library search program.  $CH_3CHO$  and nonanal were not quantitated. Breakthrough under laboratory and field sampling conditions was evaluated. Breakthrough parameters and GCMS quantitation limits are summarized in Table II. Mean concentrations of airborne carbonyls estimated from GCMS analysis is presented in Figure 5. The field breakthrough percentage for the carbonyls using Tenax method was above 35% and accordingly the reported values should cautiously be viewed with the aid of the propagated error as the minimum estimated concentrations in the study

environment. Details of the performance of Tenax TA for field sampling and GCMS analysis of other airborne volatile organic chemicals such as chlorohydrocarbons, aliphatics, aromatics, esters, and terpenes will be presented elsewhere.

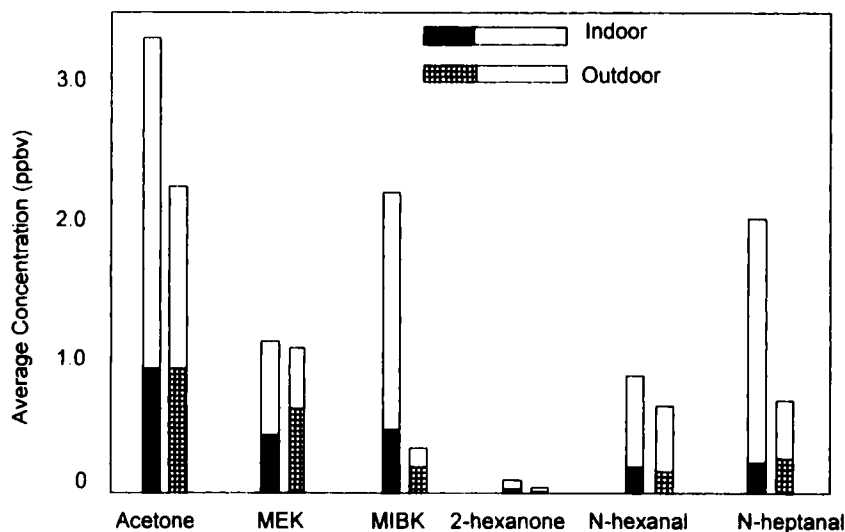


FIGURE 5 Average indoor and out door concentrations of acetone, MEK, MIBK, 2-hexanone, n-hexanal and n-heptanal from Tenax TA®-GCMS method

## DISCUSSION

### HPLC analysis

Air sampling using DNPH coated silica gel cartridges allowed the collection of low molecular weight C1-C3 carbonyls (HCHO, CH<sub>3</sub>CHO and acetone) and quantitative estimation of airborne concentration by HPLC analysis (Table II). Duplicate sampling data (both in indoor and outdoor) demonstrated DNPH cartridges can be used for field sampling to yield reproducible estimation of ambient HCHO concentrations in the office environment, within *ca.* 10%. Minimum background level in the sampling media was very important for the estimation of HCHO and acetaldehyde in indoor/outdoor of the large office environments (2 to 15 ppbv, Table IV). The 'in-series' sampling data and estimated carbonyl concentrations (C1 – C3) in our large buildings (Table III) demonstrate that the 8

hours sampling consumed only 8 to 12% of 500  $\mu\text{g}$  DNPH-reagent. 500  $\mu\text{g}$  DNPH coated blank cartridges had  $33 \pm 29$  ng HCHO, and  $56 \pm 36$  ng  $\text{CH}_3\text{CHO}$ . Comparatively, a round robin testing of commercially available DNPH-coated silica cartridges (1000 to 3000  $\mu\text{g}$  load,  $n = 33$ ) had an average blank levels of  $130 \pm 60$  ng and  $180 \pm 126$  ng of HCHO and  $\text{CH}_3\text{CHO}$  respectively [29]. The use of 500  $\mu\text{g}$  DNPH-load to reduce the background concentrations for C1 – C3 carbonyls in the sampling media did not lead to significant loss of target analytes by breakthrough (Table II).

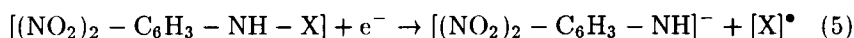
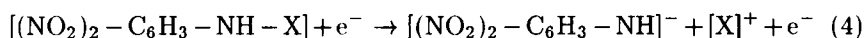
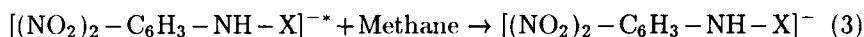
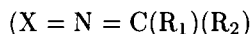
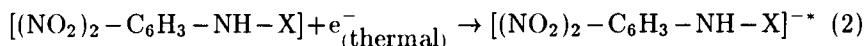
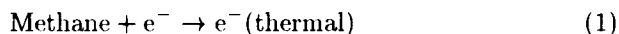
The chromatographic peak eluted immediately before product peak **1**(**X**, Figure 1) was previously observed [29, 38–39]. We also observed **X** from both ‘front’ and backup cartridges (‘in-series’ sampling, Figures 1 and 2). Grosjean and his co-workers predicted the product **X** ( $\lambda_{\text{max}} = 310$  nm) has resulted from the reaction of DNPH with ozone, NO or  $\text{NO}_2$  gases. However, we were unable to observe the complete elimination of the chromatographic peak intensity for **X** for indoor samples that contained potassium iodide cartridge, an ozone-scavenger [29, 33]. The chromatographic peak intensity change for **X** ( $21.6 \pm 10.2\%$ ,  $n = 2$  from 3 trials) was not significantly different from the total co-efficient of variation resulting from duplicate sampling and analysis of indoor samples.

### GCMS of DNPH-extracts

Grosjean and his co-workers were unsuccessful in their attempt to identify the product **X** by HPLC-MS studies [39]. Our attempt with positive ion GCMS analysis of field samples was not successful towards an unambiguous identification of target analytes and **X**. This is primarily due to low concentration of target analytes (*ca.*  $< 0.2$  ng per analysis), lack of ion-intensity for molecular ions and their fragmentation ions (Figure 3). Positive ion GCMS analysis, however, unraveled the presence 1, 3-dinitrobenzene in the blank and field sample. Kallinger and Niessner used positive ion GCMS technique and identified DNB as a major decomposition product resulting from the degradation reaction of DNPH-reagent with ozone [33].

We have tentatively identified the decomposition products such as DNB, DNP (**5**) and DNA (**6**) from the use of HPLC and further characterized by negative ion GCMS analysis (Figures 1, 2 and 4). In general, negative ion GCMS is better suited for the nitrophenyl compounds because  $\text{NO}_2$ -groups have a greater affinity for the electron [41]. Molecular ions for DNPH and its derivatives are generated through associative resonance electron capture mechanism as shown in equations 1 to 3. Base peak ( $m/z = 182$ ) and other fragmentation ions are gener-

ated through both ion pair production (most predominant, equation 4) and dissociative resonance capture mechanisms (equation 5).



Degradation of DNPH coated onto silica gels due to humidity,  $\text{NO}_2$  and ozone is known [17, 33, 40]. DNB, 5-nitrobenzofurazan, 1,3-dinitrophenylazide, DNP and DNA were identified from the reaction of DNPH with  $\text{NO}_2$  in the annular denuder sampling system [33]. GCMS (positive ion and negative ion) was able to separate **E**- and **Z**-isomers of synthetic DNPH-adducts derived from  $\text{CH}_3\text{CHO}$  and MEK (Figure 4). HPLC analysis of field samples yielded **Z**-isomer only. The unsymmetric carbonyls are known to react with DNPH to provide both kinetically stable **E**-isomer and thermodynamically stable **Z**-isomer [42].

### Tenax-GCMS

Tenax GCMS sampling allowed the positive identification of  $\text{HCHO}$ ,  $\text{CH}_3\text{CHO}$ , acetone, MEK, MIBK, hexanal and heptanal in indoor environment. GCMS analysis of Tenax TA cartridges suggest the method has limitations for quantitative analysis of hexanal (0.2 ppbv) and heptanal (0.2 ppbv), mainly due to co-elution of hexamethyl cyclotrisiloxane and octamethyl cyclotetrasiloxane that were identified from the WILS spectral library search. Tenax method allowed the identification and qualitative estimation of MEK and MIBK. MEK concentrations were  $0.4 \pm 0.7$  ppbv and  $0.6 \pm 0.4$  ppbv in indoor and outdoor near air-intake environments respectively. MIBK were  $0.5 \pm 1.7$  ppbv and  $0.2 \pm 0.1$  ppbv in indoor and outdoor near air-intake environments respectively. Estimated acetone levels by HPLC and GCMS were distinctly different due to variations in background level of acetone in sampling cartridges and inefficient trapping of acetone in Tenax TA.

TABLE IV Mean indoor and out door concentrations (ppbv) of C1-C3 carbonyls (HCHO, CH<sub>3</sub>CHO and acetone) for the fall, winter, spring and summer (November 1996 – October 1998)

Season	Fall (mean $\pm$ 1 std.dev.)		Winter (mean $\pm$ 1 std dev.)		Spring (mean $\pm$ 1 std dev.)		Summer (mean $\pm$ 1 std dev.)		2 year mean conc., (mean $\pm$ 1 std dev.)	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
Carbonyl										
Formaldehyde	5.2 $\pm$ 3.0	1.9 $\pm$ 1.1	6.2 $\pm$ 2.7	1.9 $\pm$ 1.5	5.4 $\pm$ 1.9	1.7 $\pm$ 0.7	11.2 $\pm$ 4.9	2.7 $\pm$ 1.6	7.0 $\pm$ 4.7	2.1 $\pm$ 5.1
Acetaldehyde	1.9 $\pm$ 1.2	1.6 $\pm$ 1.2	2.7 $\pm$ 0.9	2.7 $\pm$ 1.2	2.5 $\pm$ 0.6	2.3 $\pm$ 1.2	4.0 $\pm$ 1.9	2.9 $\pm$ 1.2	2.8 $\pm$ 2.0	2.4 $\pm$ 2.9
Acetone	4.1 $\pm$ 3.0	2.1 $\pm$ 1.8	3.1 $\pm$ 2.5	0.9 $\pm$ 0.3	4.8 $\pm$ 2.0	1.4 $\pm$ 0.4	7.9 $\pm$ 5.0	2.0 $\pm$ 1.4	5.0 $\pm$ 4.6	1.6 $\pm$ 4.9
Total $\Sigma_{(C=O)}$	11.2 $\pm$ 4.4	5.6 $\pm$ 2.4	12.0 $\pm$ 3.7	5.5 $\pm$ 2.0	12.6 $\pm$ 2.8	5.4 $\pm$ 1.5	23.1 $\pm$ 7.3	7.5 $\pm$ 2.4	14.8 $\pm$ 6.9	6.1 $\pm$ 7.7

### Carbonyls Distribution

Concentrations of HCHO, CH<sub>3</sub>CHO and acetone from individual buildings are reconstructed in Figure 6. The data suggest that building DM1-IA had relatively higher concentration of carbonyls than building SP1-MN and DM2-IA. Total carbonyl concentrations ( $\Sigma_{CO}$ ) were  $15.6 \pm 7.0$  ppbv and  $6.9 \pm 5.1$  ppbv in indoor and outdoor near air-intake environments respectively. Mean concentration of carbonyls in indoor and outdoor from 23 measurements covering four seasons over a 2 years period were: HCHO,  $6.8 \pm 8.8$  and  $2.1 \pm 3.1$  ppbv; CH<sub>3</sub>CHO,  $2.8 \pm 3.2$  and  $2.2 \pm 2.4$  ppbv; and acetone  $4.7 \pm 8.9$  and  $1.4 \pm 3.1$  ppbv respectively (Figure 7). Indoor to outdoor concentration ratios of 3.2, 1.3 and 3.4 for HCHO, CH<sub>3</sub>CHO and acetone clearly indicate the accumulation of HCHO and acetone from indoor material-sources, while CH<sub>3</sub>CHO concentrations indoor and outdoor were very similar. The mole distribution ratio for HCHO, CH<sub>3</sub>CHO and acetone were 47%, 20% and 33% in indoor and 37%, 38% and 25% in outdoor respectively. Rhine valley (Germany) pollution study in summer 1992 found day time HCHO concentrations in the range 1.0 to 3.6 ppbv with mole distribution ratio 37%, 14% and 49% for HCHO, CH<sub>3</sub>CHO and acetone, respectively [17].

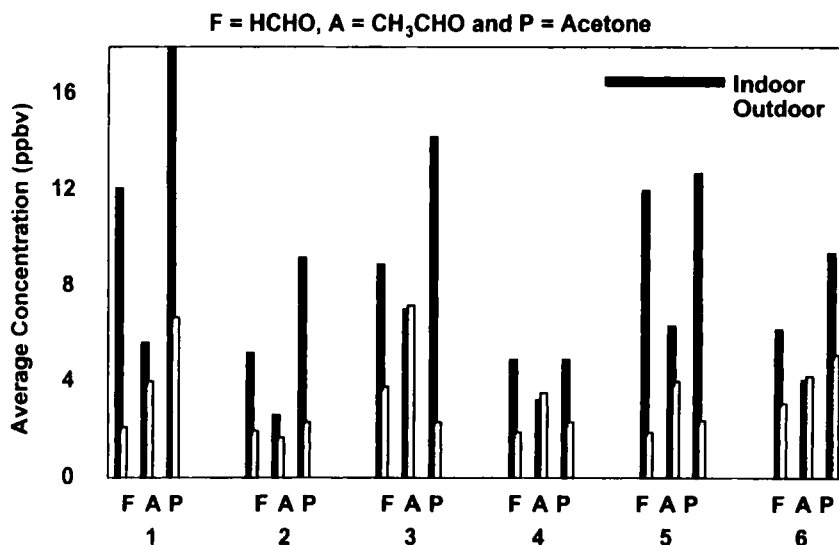


FIGURE 6 Average indoor and out door concentrations of C1 – C3 carbonyls from individual buildings

Seasonal average concentrations for the fall, winter, spring and summer are presented in Table IV. Total concentration of HCHO, CH<sub>3</sub>CHO and acetone

( $\Sigma_{C=O}$ ) were  $14.7 \pm 6.9$  ppbv in indoor and  $6.0 \pm 7.7$  ppbv and outdoor environments respectively. Mean indoor concentrations of C1 – C3 carbonyls ( $\Sigma_{C=O}$ ) were  $12.0 \pm 3.7$  and  $23.1 \pm 7.3$  ppbv during winter and summer respectively [Table IV]. Reiss and his co-workers have studied the carbonyls distribution in Boston (Massachusetts, USA) during summer and winter and reported the mean concentration of total carbonyls ( $\Sigma_{C=O}$ ) as 36.6 ppbv and 31.7 ppbv for summer and winter respectively, in residential environment [43]. In a similar study, Chang and his co-workers have identified 9 different aldehyde species with  $\Sigma_{C=O}$   $62.6 \pm 21.8$  ppbv in indoor and  $19.1 \pm 10.9$  ppbv in outdoor [44].

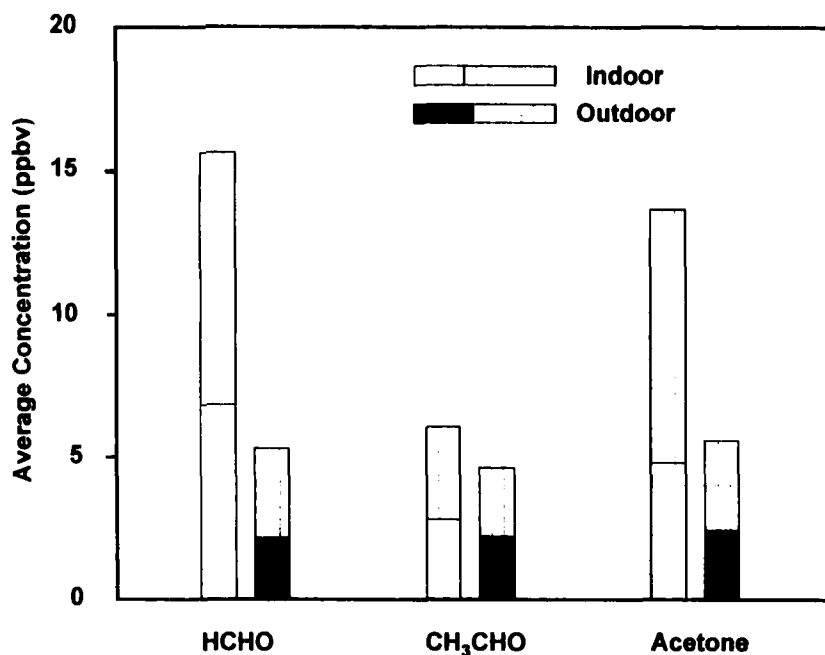


FIGURE 7 Mean Indoor and out door concentrations of C1 – C3 carbonyls from 23 sampling events covering four seasons over a 2 years period (November 1996 – October 1998)

HCHO and CH<sub>3</sub>CHO are identified in the environment close to drinking water plants where the water is treated by ozonolysis [45–49]. Other disinfection by-products (DBP) such as hydroxy-aldehydes, ketones and keto-acids have been identified from ozonolyzed water [46]. Mono- and di-aldehydes have been identified in the environment close to pilot-scale and full-scale ozonation treatment plants. Inefficient carbon packed filtration techniques will result in aerosolization of carbonyls and their derivatives from hot water faucets and

showers [49]. The presence of ozone indoors and its interaction with latex paints is another source for the generation of HCHO, CH<sub>3</sub>CHO, acetone and CH<sub>3</sub>COOH [15]. We observed styrene (0.2 ppbv) and limonene (4 ppbv) in all buildings and these two chemicals are known to react with ozone in indoor environment and generate HCHO and HCOOH [50].

Total concentration of C1 – C3 carbonyls reported in this study is lower than the concentration levels reported for urban environment [43–44] and estimated HCHO levels in non-complaint office buildings is approximately 10 times lower than the guidelines [51]. High concentration of carbonyls in the range 150 ppbv was reported in the Los Angeles area where automobile exhaust pollution is prevalent [52]. In a study conducted in 1996, carbonyl concentrations of 22 ppbv in the Los Angeles urban locations and 3.5 ppbv at the background level were reported [39] with the average HCHO concentration of 5.3 ppbv with CH<sub>3</sub>CHO/HCHO concentration ratio 0.75. Comparatively, HCHO concentration of 0.1 – 0.3 ppbv has been reported in a pristine marine environment where methane is the major source of HCHO [53]. Average HCHO levels (7ppbv) in the non-complaint buildings were much lower than the recommended concentration levels in indoors of residential home environment, 100 ppbv [54].

## SUMMARY

C1 – C3 carbonyls from indoor and near the air intakes of the non-complaint office buildings were collected using DNPH coated silica gel cartridges and analyzed by reverse phase HPLC. An excess DNPH-reagent (> 88%) was present from the use of 500 µg DNPH-cartridges following 8 hours sampling, even though DNA, DNP and DNB were observed. In addition, 500 µg DNPH-load reduces the background carbonyls with no deleterious effect on the trapping efficiency. HCHO (7 ppbv), CH<sub>3</sub>CHO (2 ppbv) and acetone (5 ppbv) were present in indoor. Outdoor environment close to the air-intake of these large buildings had HCHO (2 ppbv), CH<sub>3</sub>CHO (2 ppbv), and acetone (2 ppbv) for acetone respectively. MEK (0.6 ppbv), MIBK (0.2 ppbv), n-hexanal (0.2 ppbv) and n-heptanal (0.2 ppbv) were also identified by GCMS analysis. Estimated C1 – C6 carbonyl concentrations ( $\Sigma_{co}$ ) were  $15.6 \pm 13.2$  ppbv and  $6.9 \pm 5.1$  ppbv in indoor and outdoor environments respectively. C1 – C3 carbonyls ( $\Sigma_{co}$ ) were  $14.8 \pm 6.9$  ppbv and  $6.1 \pm 7.7$  ppbv in indoor and outdoor environments respectively. Average HCHO levels (7ppbv) in our study buildings were much lower than the recommended concentration levels in indoors of residential home environment, 100 ppbv.



### Acknowledgements

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