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VOLATILE ORGANIC COMPOUNDS IN THE AIR OF CANADIAN BUILDINGS WITH SPECIAL REFERENCE TO WET PROCESS PHOTOCOPYING MACHINES

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Volatile organic compounds in the indoor air of Canadian buildings has been measured since June 1986. Samples taken in custom 3 component sorption tubes were thermally desorbed and measured for the total volatile organic compounds (TVOC) using a flame ionization detector while simultaneously chromatographically fingerprinting the components using a gas chromatograph/mass spectrometer (GC/MS). The indoor air of each building had a specific fingerprint, however, one type of fingerprint caused by wet process photocopying machines was found in 18 of the 28 buildings studied. Copier vapour in 8 buildings amounted to more than 90% of the TVOC's. Short branched alkanes of carbon numbers 10 and 11 were the major components of the copier exhaust vapours. Analysis by atmospheric pressure chemical ionization tandem mass spectrometry showed that several non-hydrocarbon compounds were also present.

INTRODUCTION

Volatile organic compounds (VOC) include a variety of airborne organic compounds, sources of which are building materials, building contents and human activities. Twenty-eight buildings including office buildings, laboratories, libraries, hospitals, schools and other types of buildings were studied. Many of them were located in Ottawa, others were located in several other Canadian cities. Most studies were initiated by an outside request concerning buildings where there were indoor air quality (IAQ) problems.

Since the VOC occurred generally in low concentrations that were below the level detected by direct gas chromatographic analysis, commercially available sorption tubes were used for concentration during sampling. Approximately 200 air samples were taken. The trapped compounds on the sorption tubes were thermally desorbed for analysis.

Since the major component of VOC observed in Canadian buildings originated from wet process type photocopying machines[1], a further study on the components of their vapour has been performed.

During the inspection of buildings and copying machines in the buildings, it was observed that the majority of the wet process type copying machines were supplied by one manufacturer. These copying machines use two liquids for operation. Components of the vapours of these liquids were analyzed using a GC/MS. The exhaust air of one of the widely used types of copying machine was continuously analyzed using an atmospheric pressure chemical ionization (APCI) tandem mass spectrometer, an ozone analyzer, and a hydrocarbon analyzer.

EXPERIMENTAL

Sampling, quantification and GC/MS analysis

The sampling method and instrumental conditions are described elsewhere[1]. The decision on the sampling locations within the building, and the number of samples were made by the group that requested the air analysis. That group was instructed, however, not to sample in the vicinity of known VOC sources.

The sorbed VOC in the tube was quantitated by FID. Identification of compounds was performed by a) comparison with standard chemicals of commercial products, and b) MS library search.

Samples of copying machine liquids were obtained from the field. Head space vapours in containers of the liquids were analyzed by GC/MS.

Direct instrumental analysis of copying machine exhaust

Vapours generated from a copying machine in operation were monitored by an ozone analyzer, a hydrocarbon analyzer, and a tandem mass spectrometer. Details of the equipment are as follows.
. Ozone analyzer - Dasibi Model 1003-pc[1]
. Hydrocarbon analyzer - Beckman Model 400 using a hydrogen flame ionization detector
. Tandem mass spectrometer - SCIEX Model TAGA6000 APCI/MS/MS
The copying machine was operated periodically; 10 copies of a 8.5" X 11" page text were produced in a continuous operation of approximately 2 minutes duration and the machine was left in a stand-by state until the next operation. The operation started at 5, 21 and 31 minutes.

Exhaust vapours from the machine were drawn into the ozone analyzer and the hydrocarbon analyzer with Teflon tubing of 4 mm i.d. The internal pump of the ozone analyzer sampled the exhaust at a rate of 2 L/min. An external pump was used to sample the exhaust for the hydrocarbon analyzer at a rate of 2 L/min. The tandem mass spectrometer was equipped with an internal pump and sampled the exhaust at a rate of 50 L/min through a corrugated polyethylene tube of about 25 mm diameter.

RESULTS AND DISCUSSION

Compounds frequently identified in the indoor air of Canadian buildings are summarized in Table 1.

Table 1 Identified compounds in indoor air

Chloro-compounds:	$CHCL_3$, CH_2CL_2, $C_2H_3CL_3$, $C_2H_2CL_4$, C_2CL_4, C_2CL_6, Dichlorobenzenes
Freons:	CCL_2F_2, $CHCLF_2$, CCL_3F, $C_2CL_3F_3$, $C_3H_2CLF_5$
n-Alkanes:	C_4 - C_{16}
i-Alkanes:	C_4 - C_{14} especially C_8 - C_{12}
Alkenes:	C_3 - C_6
Aromatics:	Benzene, Toluene, Xylenes, C_3-C_6 substituted benzene
Alcohols:	Methanol, Ethanol, Propanols, Butanols
Aldehydes:	C_2 - C_8 aldehydes
Ketones:	Acetone, Methylethyl ketone
Esters:	Ethylacetate, Butylacetate
Others:	Methoxyethanol, Pinene, Camphene, Limonene

The TVOC normally ranged from 0.1 to 4 mg/m^3; background values (clean outside air) were

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[1] Some commercial equipment is identified in this paper to adequately describe the experimental procedure. Such identification does not imply recommendation or endorsement by the National Research Council, nor does it imply that the equipment identified is the best for the purpose.

pproximately 0.1 mg/m³. In 10 buildings, the TVOC was higher than 10 mg/m³, and in four different buildings values of 79, 83, 88 and 98 mg/m³ were found. The threshold where complaints start was reported to be 2 mg/m³[2].

Indoor air produced a specific fingerprint on a GC/MS chromatogram when analyzed by the present method. The fingerprint is specific to a building and remains the same in different locations and over time. One type of fingerprints was found repeatedly in different buildings, the source being wet process photocopying machines. In 18 of the 28 buildings studied, the fingerprint of copying machine exhaust was found. Percentages of the copier vapour in the TVOC were estimated from peak area in the chromatograms. In 8 buildings, the copier vapour amounted more than 90% of TVOC. Table 2 summarizes the results of the study.

Table 2 TVOC and percentage of copier vapour in various buildings

Building use	No. of Samples	Average TVOC mg/m³	Highest TVOC mg/m³	Percentage of Copier Vapour
Office #8	1	2.7	2.7	28
Office #7	4	17	23	67
Mall	3	0.3	0.4	0
Factory/office	6	0.4	0.9	0
Hospital #6	17	6.5	83	0
Hospital #5	16	2.2	23	0
Printing shop/office 3rd test	4	26	29	>90
Printing shop/office 2nd test	6	3.4	3.9	90
Hospital #4	17	1.3	4.6	0
Hospital #3	3	20	98	16
Office #7	4	8	88	>90
Warehouse	11	1.8	3.9	27
Office #6	5	0.7	2.8	80
Office #5	4	0.8	2.4	32
Library #2	3	8	13	>90
School #2	12	2.4	5.3	>90
Conference centre	3	2.5	4.2	0
Hospital #2	3	0.3	0.4	0
Hospital #1	5	0.7	1.3	0
Office #4	4	0.1	0.4	0
School #1	8	2	5.9	80
Office #3	2	0.5	3	70
Office #2	14	4	19	>90
Printing shop/office	3	3	6.4	>90
Office #1	7	0.4	13	>90
Office/laboratory #5	3	1.2	6.2	30
Office/laboratory #4	1	0.2	0.2	0
Office/laboratory #3	1	0.1	0.1	50
Office/laboratory #2	1	0.2	1.8	0
Library #1	24	11	79	>90
Office/laboratory #1	4	1.6	10	>90

The wet process copying machine in this study uses two liquids: dispersant (Liquid #1), and a toner (Liquid #2). According to information obtained from the manufacturer of the wet-process type copying machines and the manufacturer of the solvent used for the liquids [3], both copying liquids use the same solvent. The solvent is an essentially odourless clear liquid of specific gravity 0.75 and boiling range 155-176°C made by the hydrotreatment of heavy naphtha.

The GC/MS analysis of the head space vapour of Liquid #1 is shown in Fig. 1. Retention of spiked normal alkanes of carbon numbers 9 to 11 are also shown in the figure. The components of Liquid #1 were distributed mainly between n-nonane and n-undecane. The GC/MS analysis results of Liquid #2 were similar to #1, but the components were distributed mainly between n-decane and n-undecane. It is understood that, in the process of preparing Liquid #2, the lower molecular weight components of the solvent are vaporized. In Fig. 2, a typical VOC fingerprint of building air containing copier vapours is shown.

Figure 1 GC/MS analysis of Liquid #1

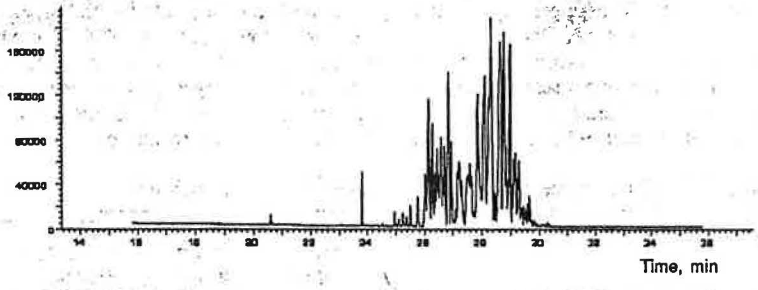
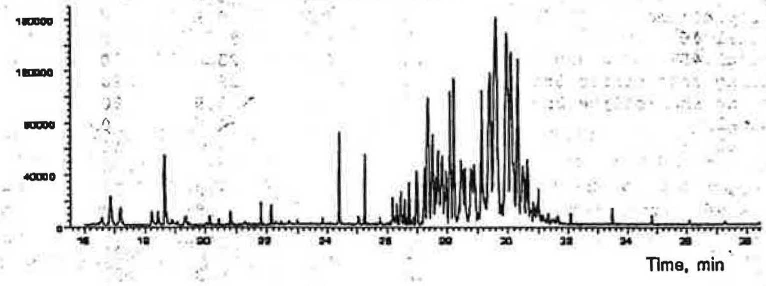


Figure 2 GC/MS analysis of volatile organic compounds in indoor air



In the mass spectra of unknown peaks obtained in the GC/MS analysis of the Liquid #1 vapour, ions of M/e, 43, 57, 71, 85, 99 were prominent. The series is caused by ions of CnH2n+1, n being mostly from 3 to 7 and some 8. This series of ions can be produced by fragmentation of alkanes [4]. Since chain scission is preferred at the branching site, n would be related to the length of the longest carbon chain without a branch.

GC/MS analysis of standards, n-alkanes (n=9, 10, 11, 12) and three monomethyl decanes (2-, 3-, 4-) were compared with those of the copier liquids. These standards had similar retentions to those in the copier fluids, but none of the retentions or mass spectra agreed.

Library searches of spectra in the chromatogram of Liquid #1 were performed on the 10 highest peaks and the 5 best library fits were recorded. This yielded 50 compounds with some duplications; all were branched alkanes. Among the compounds of best fit were alkanes with two or more methyl branches and, if more than two, two methyl branches belonged to the 2-position of the trunk carbon chain. In the library search of the spectrum of the highest peak, the best fit was 2,2,6-trimethyl octane.

There were 3 peaks in the single ion chromatogram (M/e=91) of Liquid #1. These were identified as the isomers of xylene, total quantity was 0.015% of the solvent.

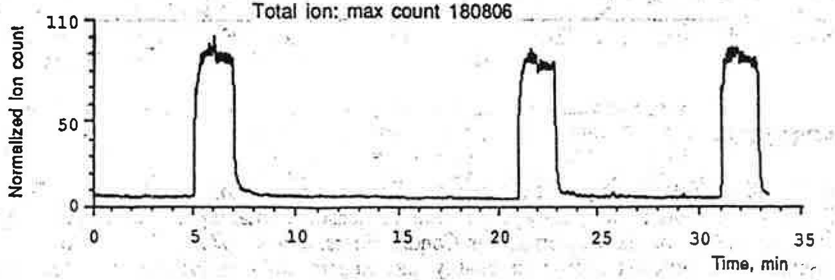
By APCI only polar molecules are seen and the matrix of hydrocarbons, which obscures interesting but minor components, is not seen. In Table 3, the major parent ions of the copying machine exhaust in the positive mode of the APCI/MS/MS are shown. In the positive mode, ions are MH+ where M is a molecule, and H is hydrogen atom, that is, mass/charge ratio (M/Z) is molecular weight +1. Possible compounds and maximum ion counts are also shown in the table.

Table 3 Parent ions and their maximum counts in APCI/MS/MS (positive mode) analysis of photocopier exhaust

M/e	compounds (1)	max.ion counts	max. conc (ppb)
57	fragment		
59	acetone	31623	6
70		10100	
71	fragment of O-comp	58200	
85			
101	methyl methacrylate	41704	6
121	DEG monomethylether	9502	4
127		11502	
137	NC-$(CH_2)_6$-CN	35496	5
155		9802	

(1) Identified by library search

Figure 3 Time profile of total ion in APCI/MS/MS (positive mode) analysis of photocopier exhaust

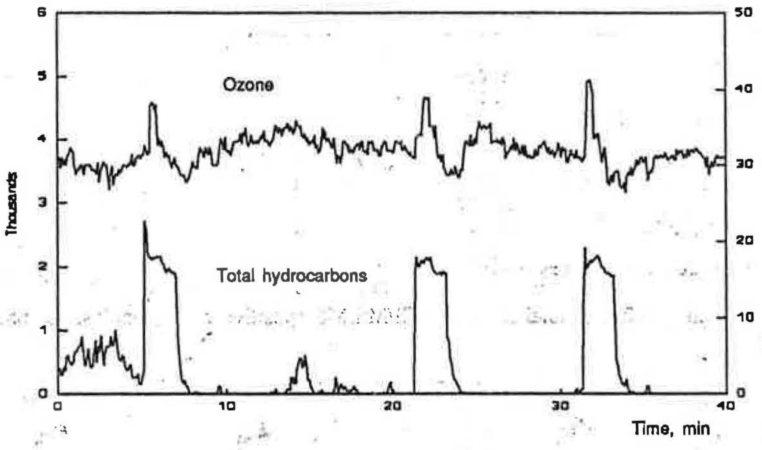


When the machine was making copies, ion counts in the exhaust were high. Fig. 3 shows the total ion count profile. Ions M/Z= 70, 71, 101, 121, 127, 137, and 155 also had the same profiles but are not shown. It is notable that non-hydrocarbon compounds were produced while the photocopier was producing copies but they were not while the photocopier was in stand-by. In Fig. 4, concentrations of total hydrocarbons and ozone are shown. The observed maximum concentration was 3 g/m^3 and 40 ppb respectively. The threshold limit value of ozone is 100 ppb[5].

CONCLUSION

Volatile organic compounds in indoor air of Canadian buildings were studied by sorption tube sampling, quantification by FID and fingerprinting by GC/MS. Groups of volatile organic compounds were identified. The TVOC ranged from 0.1 to 98 mg/m^3. A significant quantity of vapours from wet type photocopying machines was found in 18 of 28 building studied. These copying machines use two liquids, #1 and #2. The main components of Liquid #1 were branched alkanes mostly of carbon numbers 10-11, while those of Liquid #2 were mostly carbon number 11. The components did not include n-alkanes or monomethyl alkanes. All components had prominent ion fragments C_nH_{2n+1}, n being mostly from 3 to 7 and some 8. Ten major components were searched in the spectral library; compound of best fit for the highest peak was 2,2,4-trimethyl octane, best fits for other peaks were branched alkanes. The content of aromatic hydrocarbons was less than 0.02%. While the copying machine was in operation, hydrocarbon vapour was produced, the maximum concentration of which was 3 g/m³. Besides the high concentration of hydrocarbons, ozone and several organic non-hydrocarbon compounds, which were mainly oxygenated compounds, were also produced.

Figure 4 Total hydrocarbons and ozone in photocopier exhaust



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