VOLATILE ORGANIC COMPOUNDS IN CANADIAN INDOOR AIR

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Volatile organic compounds (VOC) in Canadian indoor air have been measured during the past 7 years, sampling by sorbent tubes, quantification of total VOC by a flame ionization detector (FID), and identification and quantification of individual compounds by a gas chromatograph/mass spectrometer (GC/MS). Stored data are analyzed by drawing 26 single ion chromatograms. Total quantities of volatile organic compounds (TVOC) and frequently detected compounds are presented.

Introduction

Since June 1986, volatile organic compounds have been measured in the indoor air of Canadian buildings. Such measurements were often prompted by air quality problems in buildings. Samples were taken in 3-layered sorbent tubes and trapped compounds were thermally desorbed into the helium stream of an analytical system. TVOC were measured using a FID while simultaneously chromatographically fingerprinting the components using a GC/MS. The resulting analytical data were stored in a data system. Selected organic compounds were identified and quantified in these data files to determine the background level of the compounds in Canadian indoor air. The compounds selected for measurement included several halogenated compounds, oxygen compounds, terpenes, and alkanes of carbon numbers from 8 to 16. Thirty-two workplace buildings and 13 houses were initially studied and more buildings are presently being studied. Multiple samples were usually collected in a building. Only one sample file, the one considered to best represent the building, was selected for this work. Most of the organic components present were observed in every part of the building, whereas samples taken in the vicinity of a known source were enriched with some contaminating compounds. Such sample files were not included in this study. A sample from the return air of an air circulation system was considered to be one of the most representative samples.

Quantitative data will be presented for each compound separately using a percentile expression. "A percentile is a value in the range of a set of data which separates the range into two groups such that a given percentage of the measures lie below this value"[1].

The authors previously presented quantification of TVOC and individual VOCs[2]. Methods for identification and quantification of these have been improved and new data have been added. Recent information will be presented in this paper.

Experimental

Air sampling locations within buildings and the number of samples taken were decided by those requesting the air analysis. Instructions were given, however, not to sample in the vicinity of known VOC sources. Sampling was undertaken using a commercially available 3-layered (glass beads, Tenax TA[1], Ambersorb XE-340) tube, 20 cm long and 4 mm i.d. An air sample was drawn into the tube using suction from a mechanical pump. Sampling time and sampling volume were normally 20 minutes and 5 L respectively at a sampling rate of 250 mL/min. When required, the sampling time duration was extended for cleaner air or shortened for high VOC air. A blank tube

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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.

was often carried to and from the sampling site. No air was taken into such tubes and VOCs in the tube were analyzed to determine the tube background. Tubes were reused after desorption (see below) and cleaning at 280°C with a helium flow for 20 minutes.

Trapped VOCs were thermally desorbed into a helium flow using an Envirochem Unacon Model 810 desorber unit. The functions of the desorber unit were described by Chan and others[3]. The flow was split into three parts. Two 4% splits went into an FID for monitoring purposes at different times, the latter of which was used for quantification of the TVOC. The remaining 92% flow was introduced into the gas chromatograph separation column of a Hewlett Packard Model 5995 GC/MS. The column was a phenylmethyl-silicone bonded phase fused silica capillary (DB-5), 60 m long and 0.25 mm i.d. The oven temperature was programmed to operate from -50°C to 250°C at a rate of 10°C/min for GC separation. The MS was operated with electron energy of 70 Ev and a mass range of 20-300 M/e units

For the identification of components in the GC effluent, both the specific GC retention of the compound and mass spectra were used. Components were initially identified by the MS using a spectra library and search program supplied by the manufacturer of the instrument. The library contained 76,000 entries including the NIH/EPA/MSDC Mass Spectra Data Base (NBS Library) and the Registry of Mass Spectra Data (Wiley Library). The searching program used a Probability Based Matching algorithm

The specific retention was defined, in this study, relative to three reference compounds, namely, benzene, toluene and dichlorobenzene. At least two of these three compounds were detected in 99% of the field samples. The specific retention, Rt, was calculated by the following equation where D_t, B_t, and X_t are retention times of dichlorobenzene, benzene, and a compound of interest. The constant 30 was selected such that the specific retentions of most interesting compounds fell between 0 and 100.

$$R_t = 30 \times (D_t - X_t)/(D_t - B_t) \qquad (1)$$

Dichlorobenzene usually appeared as only one peak. When one of the two reference compounds were missing, the retention time of toluene and the retention times of the compound in the previous analyses were used to estimate the retention time of the missing peak.

When the calculated specific retention of a peak did not agree with the previously determined specific retention, MS identification was discarded. When they agreed, the mass spectra of the compound and the standard mass spectra drawn from the library were compared to confirm identification.

To measure concentrations of organic compounds in air samples, the response factor of the FID was calibrated by injecting known volumes of a cylindered, dilute cyclohexane vapour (Matheson certified 607 ppm cyclohexane in helium) into sorption tubes. The equation for the calculation is:

$$f = c_s/V_s/C_s \qquad (2)$$

where,
    f: response factor in count/μg
    c_s: FID count for a known volume of standard cyclohexane/helium
    V_s: Volume in m^3 of the standard cyclohexane/helium
    C_s: concentration of the standard cyclohexane/helium in μg/m^3.

The TVOC, T in μg/m^3, was then calculated as:

$$T = c/f/V \qquad (3)$$

where,

c: FID count for an air sample
V: volume in m³ of the air sample taken into the tube.

For quantification of individual compounds, a single representative ion was selected for each compound and the ion counts under a peak in the single ion chromatogram was measured. Twenty-six selected single ion chromatograms were routinely drawn to detect and quantify compounds. The single ion MS response factor for some of the compounds was experimentally measured to calculate quantities of the compounds.

For compounds whose response factors have not been measured, the total ion counts of the same compound in the total ion chromatograms were calculated from the single ion counts by regression analysis. Data for the regression analysis were taken when ion counts under a peak in the total ion chromatogram were measurable with accuracy. The single ion counts were always accurately measured.

The total ion count, I_T, was related to the single ion count, I_S, by the following equation.

$$\log_{10}I_T = A + B \times \log_{10}I_S \tag{4}$$

A and B in the equation are empirically obtained regression constants, values of which are given later in this paper.

The quantity of the compound was considered to be proportional to the total ion counts under a peak in the total ion chromatogram. The concentration was then calculated as:

$$C = T \times I_T/\Sigma I_T \tag{5}$$

where,
I_T: total ion counts under a peak in the total ion chromatogram
T: TVOC in $\mu g/m^3$
C: concentration of the component of interest, in $\mu g/m^3$

The method is not truly quantitative in that the response factor of each compound was not determined. When the response factors of an individual compound become available, the quantitative data will be revised.

Results and discussion

The specific retention has not significantly varied, except for compounds of early elution (acetone for example), in the past 7 years, although retention times for the reference compounds varied. The relationship between single ion counts and total ion counts is shown in Fig. 1 using acetone as an example. Specific single ions for compounds and the calculated results of the regression analysis, when applicable, are summarized in Table 1. As shown in the last column by the standard error of regression, the fit was good except for CCl_3F and $C_2H_2Cl_2$. The total ion chromatogram peaks for these compounds were not well separated from other peaks.

The use of single ion chromatograms was effective in quantification. It was not possible to measure the quantity of benzene, for example, on the total ion chromatogram because benzene co-eluted with cyclohexane which was used as the calibration standard. These two compounds were completely resolved in single ion chromatograms as M/e=78 and M/e=84; the former for benzene and the latter for cyclohexane. Peaks in a single ion chromatogram were normally completely resolved.

Percentages of detection and the 20, 50 and 80 percentile concentrations in $\mu g/m^3$ of various compounds are summarized in Table 2.

Frequently detected compounds include acetone, ethanol (in houses), 1,1,1-trichloroethane, dichlorobenzene, benzene, toluene, and xylenes. Wallace et al reported similar results using a Tenax absorber and thermal desorption[4]. Differences from those results are styrene (Wallace 77% detection vs 16%) and trichloroethylene (Wallace 46% vs 9%). Acetone and ethanol were not measured in Wallace et al paper. Styrene and o-xylene co-eluted in this work and, unless resorting to single ion analysis (styrene M/e=104, o-xylene M/e=106), they could not be distinguished.

Benzene is listed as a carcinogen[5]. P-dichlorobenzene is a suspected carcinogen, but this is yet to be confirmed[6]. Dichlorobenzene in this study usually appeared as single peak in single ion chromatograms of M/e=146, however, in some samples appeared as two adjacent peaks 0.03 min apart. The major peak of the two was considered as the p-isomer from the order of elution. Dichloromethane, which is also listed as a carcinogen[5], was detected in 13% of the samples. Less frequently detected compounds are listed in Table 3.

Fig. 2 and Fig. 3 show percentile concentrations of 1,1,1-trichloroethane and ethanol respectively. The observed concentrations of these compounds in workplaces and houses were substantially different. 1,1,1-trichloroethane is used for fabric protection, household products and office products[7]. Significant and diverse concentrations of copier vapours were found only in workplaces. The measured concentrations of nine selected compounds are shown in Fig. 4 to visualize relative abundance. Percentile-Concentration relations are shown by linear regression lines to avoid confusion.

TVOC in houses and workplaces with and without copier vapours are shown in Fig. 5. Fiftieth percentile values are 0.5, 0.79, and 0.87 mg/m^3 respectively for workplaces without copiers, houses, and workplaces with copiers. Workplaces had lower TVOC values than houses when there was no copier present. Turner and Binnie's data on TVOC for 26 Swiss office buildings[8] shows similar percentile curve as the TVOC without copier curve in Fig. 5. Seifert and other's data[9] on 500 German homes, obtained by passive sampler, CS2 desorption and GC analysis, shows lower values (0.33 mg/m^3 50-percentile). Background values in the present work measured with clean outside air were approximately 0.1 mg/m^3.

References

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TABLE 1. Specific single ion and regression constants to calculate the total ion count

Compounds	Specific single ion	Regression constants A	B	Std. error
Acetaldehyde	44			
Acetone	58	1.07744	0.95164	0.03426
Ethanol	45	1.20296	0.91810	0.04533
CH_2Cl_2	84	0.14373	1.14434	0.00625
CCl_3F	101	0.08658	1.09864	0.1257
C_2H_5Cl	64			
$C_2H_2Cl_2$	96	1.25229	0.74015	0.3075
$C_2H_4Cl_2$	62			
C_2HCl_3	30			
$C_2H_3Cl_3$	97	0.14165	1.1075	0.06904
C_2Cl_4	129	0.86935	1.02475	0.08980
C_2HCl_5	83			
$C_2Cl_3F_3$	151			
C_3H_7Cl	42			
$C_3H_6Cl_2$	63			
$C_3H_5Cl_3$	110			
Propane	43			
Dichlorobenzene	146	0.35630	1.03399	0.03975
Benzene	78	0.31654	1.0010	0.07934
Toluene	92	0.47394	1.0199	0.06827
Xylene	106	0.89038	0.98329	0.04362
Styrene	104			
Naphthalene	128			
Terpenes	136	1.90769	0.86748	0.06144
n-alkane C9-16	57	-0.0748	1.20777	0.06755
Hexanal	98			

TABLE 2. Percentages of detection and percentile concentrations in $\mu g/m^3$

Compounds	Tot. No. of samples	Percent of detection	Percentile 20	Percentile 50	Percentile 80
Acetone	45	80.0	5.37	20.9	52.8
Ethanol W	32	25.0	5.84	14.4	65.7
Ethanol H	13	69.2	52.2	141.	378.
2-Propanol	45	13.3	53.1	78.8	162.
CH_2Cl_2	45	13.3	2.8	6.56	41.4
$CHCl_3$	45	8.9	0.05	1.86	14.9
CCl_3F	45	20.0	0.445	3.25	137.
$CH_2=CCl_2$	45	13.3	0.959	3.95	4.63
CH_3-CCl_3 W	32	84.4	1.01	6.16	16.8
CH_3-CCl_3 H	13	61.5	0.202	0.783	2.33
$CHCl=CCl_2$	42	9.5	ND	2.61	30.4
$CCl_2=CCl_2$	45	51.1	0.845	3.57	25.5
Dichlorobenzene	45	68.9	0.938	3.05	14.6
Benzene	45	93.3	1.45	3.47	10.1
Toluene	45	95.6	1.41	3.48	11.7
Xylenes	45	82.2	1.39	6.83	17.2
Styrene	42	26.2	0.26	0.87	17.4
Pinene	45	8.9	ND	4.72	42.0
Limonene	45	31.1	3.64	18.1	43.4
n-Nonane	45	13.3	2.24	4.00	9.82
n-Decane	45	33.3	7.82	21.4	38.0
n-Undecane	45	33.3	3.96	31.6	77.6
n-Dodecane	45	24.4	0.843	5.14	13.8
n-Tridecane	45	17.8	0.611	2.78	6.45
n-Tetradecane	45	15.6	1.75	2.32	6.98
n-Pentadecane	45	13.3	1.30	3.42	5.40
n-Hexadecane	45	11.1	0.724	1.29	12.2
Copier W	32	40.6	37.5	436.	2075.
TVOC H	13	100.	500.	790.	2060.
TVOC W with copier	13	100.	150.	640.	2600.
TVOC W no copier	19	100.	270.	500.	1620.
TVOC H&W	45	100.	290.	624.	2320.

H: House   W: Workplace   ND: non-detectable

TABLE 3. Other compounds less frequently detected

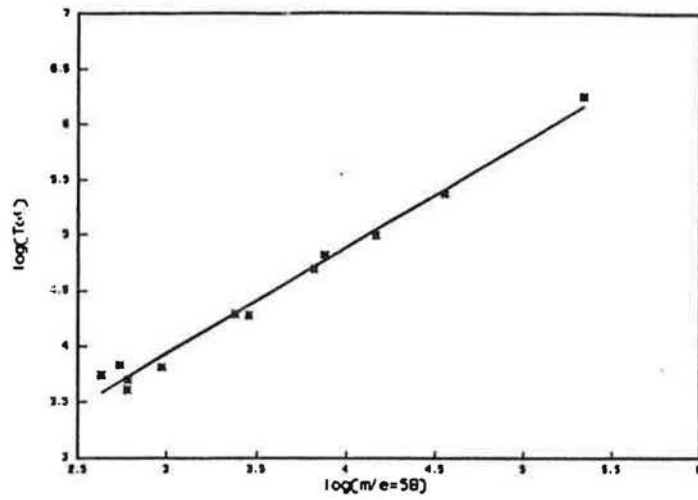| Compounds	Tot. No. of samples	No. of detections	Concentration $\mu g/m^3$
CCl_2F_2	45	1	3.98
C_2H_5Cl	45	1	11.1
$CCl_2F=CClF_2$	45	1	31.3
Acetaldehyde	45	1	21.2
Ethylacetate	45	1	28.1
Hexanal	45	1	22.6
Dimethylaminoethanol	45	1	230.
Naphthalene	45	1	22.6
Camphene	45	2	8.13

Fig. 1   Relation between single ion count (M/e=58) and total ion count for acetone
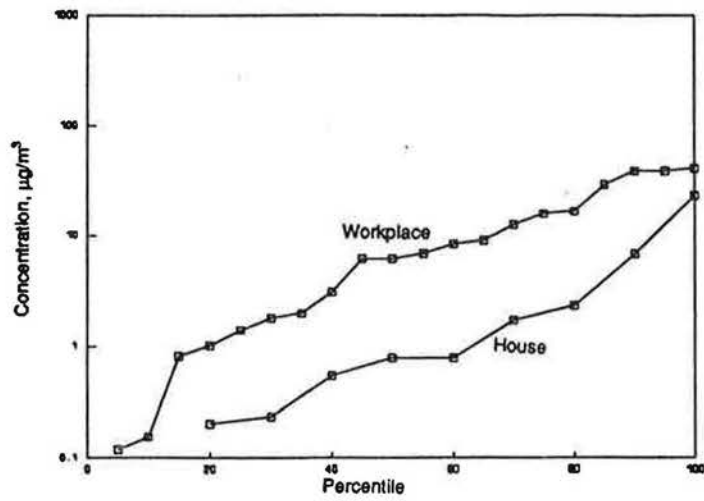

Fig. 2   Percentile concentrations of 1,1,1-trichloroethane in workplaces and houses
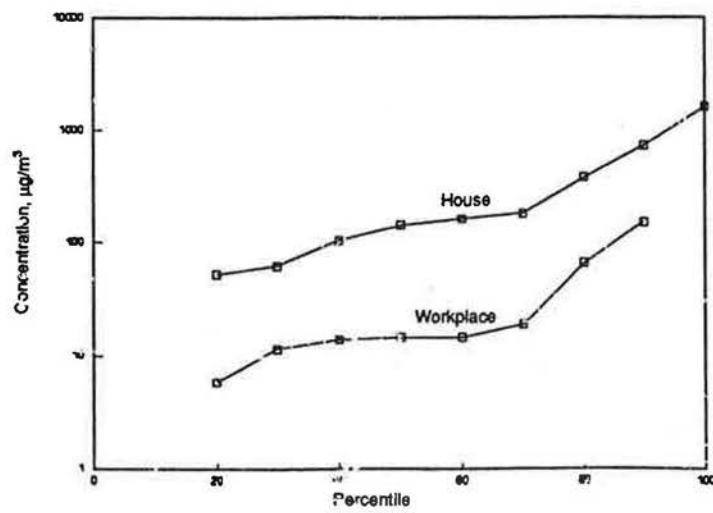

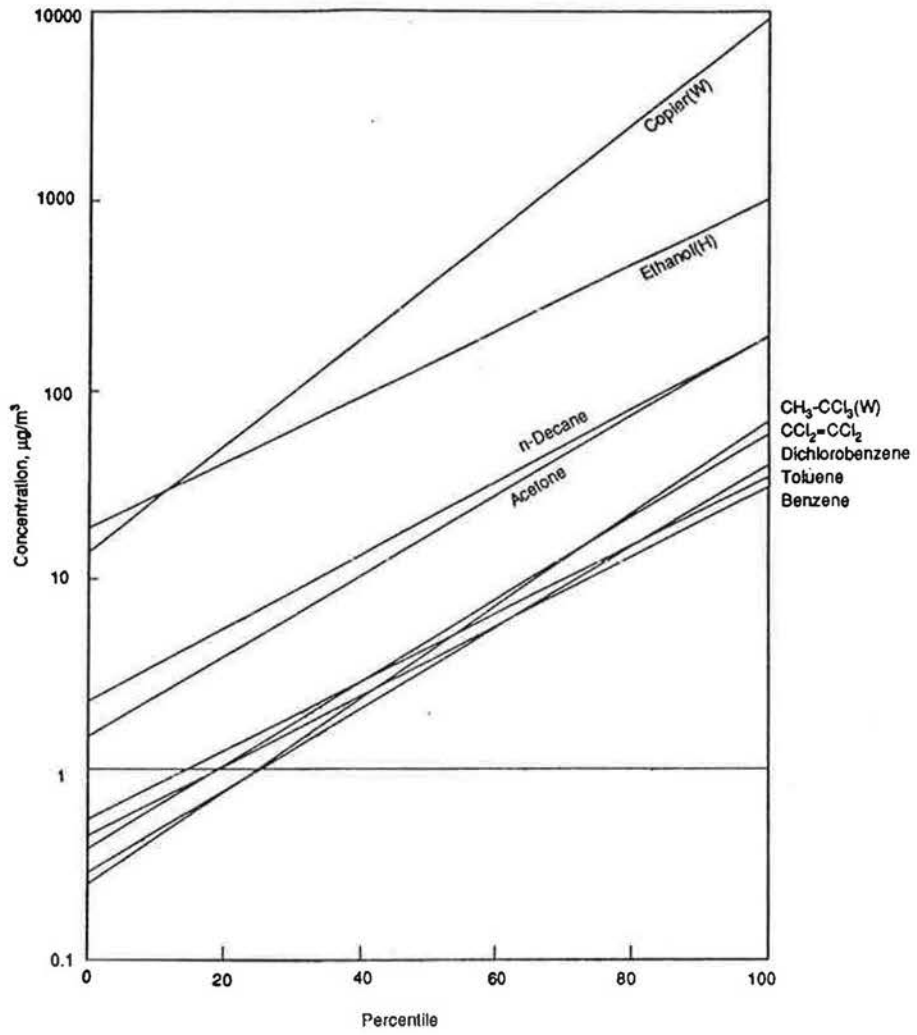Fig. 3   Percentile concentrations of ethanol in workplaces and houses
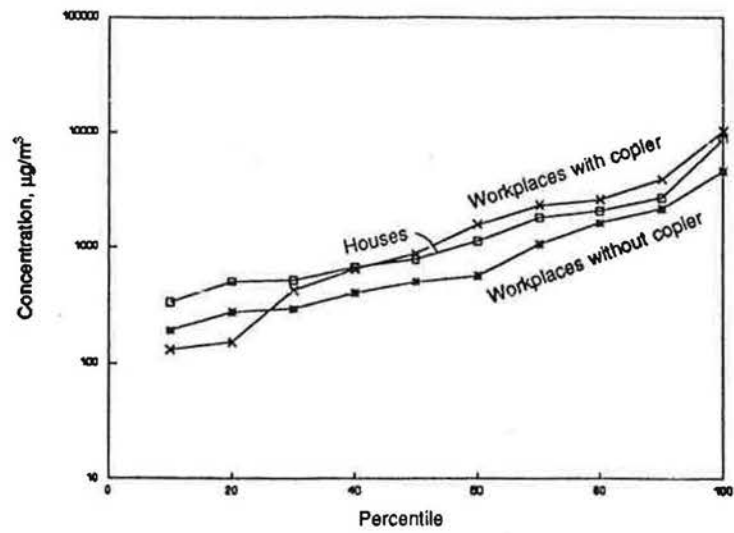
Fig. 4 Relative abundance of 9 selected compounds

Fig. 5 TVOC in houses and workplaces with or without copier vapours