Bull. Environ. Contam. Toxicol. 31, 222–229 (1983)

Survey of Selected Organics in Office Air

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Studies relating indoor air quality and organic contaminants have generally focused on the home (STEWART & HAKE 1976, WILLIAMS et al. 1981) and workplace (BRUGNONE et al. 1978, ENGSTROM et al. 1978) environments. However, office environments where small quantities of materials containing volatile ingredients are in use occasionally or in limited quantities have received limited attention (HOLLOWELL & MIKSCH 1981).

Materials such as, glues, cleaning solvents, deodorizers, type correction fluids, and coloring pens are used in many offices. Use of these materials may result in worker exposure to volatile and potentially hazardous materials, such as trichloroethane from type correction fluids. Since exposure levels cannot be predicted, health hazard assessment is difficult. To aid in the health hazard assessment of organics in office air, 30 local offices were surveyed for potential sources and the air levels of selected volatile organic compounds were determined.

MATERIALS AND METHODS

Analytical methods. Analyses at laboratory 1 (Health and Welfare Canada) were done with the aid of a Model 5840 Hewlett-Packard gas chromatograph equipped with a flame ionization detector (FID), a Model 8000 Varian automatic sample injector (autosampler), and a nickel 200 column (2.2 mm I.D., 1.8 m long) packed with 0.1% SP1000 on 80/100 mesh Carbopack C. The temperatures of the injection port and the detector respectively were 150°C and 300°C. After each injection (0.2 uL), the column oven temperature was maintained at 60°C for 3 min and was then raised at a rate of 15°C/min to 220°C where it was maintained for 11 min. Gas flows were 15 mL/min, 20 mL/min, and 250 mL/min respectively for nitrogen, hydrogen, and air. A Varian Vista Series 4600 gas chromatograph equipped with an FID, an autosampler (2 uL injections), and a CDS 401 data system with a printer-plotter was used at laboratory 2 (Forintek Canada Corp.). The chromatography column and conditions were similar to those listed above. A nickel 200 column (2.2 mm I.D., 1.8 m long) packed with 20% SP2401/0.1% Carbowax 1500 on 100/120 mesh Supelcoport was also used to aid in compound identification.

TABLE I. Composition of Standard Mixtures 1-4 & A-C.

Mixture 1 - Dichloromethane(A), Acrylonitrile(B), Chloroform(A), Methyl ethyl ketone(B), 1,1,1-Trichloroethane(C), Ethyl acetate(A), 1,1,2-Trichloroethane(B), Benzene(C), Hexane(A), Tetrachloroethylene(B), Toluene(C), Amyl acetate(A), Octane (B), o-Xylene, p-Xylene(C).

Mixture 2 - Isopropanol, Ethyl ether, Dioxane, Allyl alcohol, Methyl n-propyl ketone, n-Propanol, sec-Butanol, Ethylene chlorohydrin, n-Propyl acetate, Chlorobenzene.

Mixture 3 - Methyl formate, Acetone(C), 1,1-Dichloroethane, 1,2-Dichloroethane, Pentane, Carbon tetrachloride, Trichloroethylene, 1,2-Dibromoethane, Bromoform, 1,1,2,2-Tetrachloroethane, Mesityl oxide, Ethyl benzene, Cumene, m-Xylene.

Mixture 4 - Ethanol, Methyl acetate, tert-Butanol, Isobutanol, n-Butanol, Isopropyl acetate, Isopropyl ether, Diacetone alcohol, Benzyl chloride, Styrene.

Compound purity, retention time, detection limit, and linearity of concentration-detector response were determined by gas chromatographic analysis of solutions of individual compounds in carbon disulfide. Bulk quantities of standard mixtures, as shown in TABLE I, were prepared and sealed in autosampler vials. Each of mixtures 1 to 4 contained equal weights ($\pm$ 1%) of the components and mixtures A, B, and C contained the components in the weight ratio of their 1980 ACGIH TWA-TLV (ACGIH 1980). Standard solutions were prepared by injecting appropriate aliquots of the mixtures into sealed vials containing 4.0 mL of carbon disulfide.

Quantitative and qualitative determination of organics in air was done by the above and previously described (ABCOR 1978, DUPONT 1980, NIOSH 1977) techniques and with the aid of standard solutions. Air sampling was done by means of charcoal tubes (Lot no. 120, SKC Inc., R.D.1, PA), Pro-Tek organic vapor monitoring badges (G-AA, E.I. DuPont de Nemours & Co., Wilmington, DE), and GASBADGE organic vapor dosimeters (Abcor Development Corp., Wilmington, MA). Calibrated, Model 808 Accuhaler personal sampling pumps (MDA Scientific, Inc., Park Ridge, IL) equipped with 10 cm^3/min orifices and Tygon tubing connectors were used for the charcoal tube technique (NIOSH 1977). Badges (DUPONT 1980) and dosimeters (ABCOR 1978) were used according to prescribed techniques. Desorption efficiencies were determined by the phase equilibrium technique (DOMMER & MELCHER 1978).

Test atmosphere. A 1.01 m^3 capacity chamber (1.43 m x 0.89 m x 0.79 m) constructed from 2 mm thick, stainless steel sheet metal and with a removable glass door sealed by means of weatherstripping over a 0.5 m x 0.5 m opening was used in the test atmosphere experiments. Small ports (1 cm diameter) which could be sealed with rubber gaskets and stoppers were drilled in the wall with the glass door. A metal rod assembly supported the air sampling devices near the geometric centre of the chamber. When desired, a small electric fan (Caframo Model 707, Wiarton,

Ont.) provided an air flow of about 0.2 m/s, as measured by an air velocity meter (Model 1650, TSI Incorporated, St. Paul, MN), near the air sampling devices. A hot plate, placed under one corner of the chamber, allowed heating of a small portion of the chamber floor.

For the test atmosphere experiment, the badges and dosimeters were uncovered (activated) inside the chamber, which was then immediately sealed. Then, 500 uL of mixture 1 (TABLE I) was added, through a port, to a Petri dish on the chamber floor above the warm hot plate, the fan was started (if desired), and the external Accuhaler pumps were started. The hot plate was removed after about 10 min when no mixture was visible in the Petri dish. After 4 h, the pumps were stopped, the chamber door was removed, and the sampling devices were immediately sealed. The charcoal elements and tube sections were stored at 4°C in labelled sealed vials until the day of analysis. The sections and elements respectively were then desorbed with 1.0 mL and 2.0 mL carbon disulfide.

Survey protocol. The air quality in Ottawa offices was monitored over a 6 to 8 h period during business hours in February, 1982. A variety of businesses and buildings were selected and described. One area and two personal exposure measurements were made by means of dosimeters in each of 30 offices. Also, Pro-Tek badge measurements were obtained side-by-side with the dosimeters in 7 offices. Blank measurements (unexposed element) were obtained for dosimeters at 7 offices and for badges at one office. Office personnel removed the labelled monitoring devices and elements from their sealed containers, activated the devices for exposure measurement and either attached them to clothing near the breathing zone or placed them in a central location at a normal working level. Participants were instructed to note the start and end time of the monitoring period and to leave the activated device on their desk during brief absences from the office. For absences longer than 30 min. they were asked to leave the devices on their desk in the closed (inactive) position and to note the time they were out of the office. During the work day, the personnel completed a questionnaire which requested information on potential sources of organics and any unusual occurrences or conditions observed during the exposure period. At the end of the exposure period, the closed devices were sealed in provided containers and were then collected for transport to laboratory 2. The elements were immediately sealed in clean vials which were stored at 4°C until the day of analysis.

RESULTS AND DISCUSSION

The charcoal tube (NIOSH 1977), Pro-Tek (DUPONT 1980), and GASBADGE (ABCOR 1978) sampling devices were designed for the monitoring of volatile organics in air and for a sampling range of about 1 ppm-h to more than 1000 ppm-h. However, the performance of the devices under different conditions, such as the presence of mixtures of organics at very low levels in air

with poor circulation, has not been well defined. To aid in the evaluation of the office air survey results, the analytical performance of the passive device and charcoal tube techniques were compared under controlled conditions.

The 51 compounds shown in TABLE I were selected from listings in the passive device literature (8,9). Gas chromatography detection limits of better than 1 ng for each compound were generally obtained when carbon disulfide solutions of the standards were analyzed. Acrylonitrile (4 ng), allyl alcohol (5 ng), 2-propanol (10 ng), 1-propanol (5 ng), ethylene chlorohydrin (5 ng), 2-butanol (5 ng), ethanol (100 ng), methyl acetate (100 ng), iso-butanol (5 ng), and 1-butanol (5 ng) at laboratory 1, and chloroform (10 ng) and methyl ethyl ketone (10 ng) at laboratory 2 showed higher detection limits, mostly due to poor peak shape or poor resolution from the solvent peak. For the remaining 41 compounds, the linear correlation coefficient was generally better than 0.999 for the relationship between detector response and amount of compound injected in the range 1 ng to 100 ng. The peak area reproducibility for each compound was usually better than 5% RSD with triplicate solutions of the standards mixtures. Poor reproducibility was due to inaccurate peak area measurements by the electronic integrator. In view of some anticipated potential sources of organics in office air, 15 representative compounds were selected for more detailed investigation.

Desorption efficiencies were determined in triplicate by the phase equilibrium method (DOMMER & MELCHER 1978) for each of the three types of charcoal sorbent. Determinations with solutions of mixture 1 (0.05 mg/L) at laboratory 1 and mixtures A, B, and C (0.05 TWA-TLV) at laboratory 2 showed that desorption efficiencies were generally 1.00 $\pm$ 0.10 for the 16 compounds investigated. However, values outside this range were obtained with the Pro-Tek elements and methyl ethyl ketone (lab 1; 0.58; lab 2, 0.54), ethyl acetate (lab 1, 0.75; lab 2, 0.77), and amyl acetate (lab 1, 0.83; lab 2, 0.79), with the GASBADGE elements and methyl ethyl ketone (lab 1, 0.86; lab 2, 0.82), and with 100 mg portions of charcoal from sampling tubes and methyl ethyl ketone (lab 1, 0.72), ethyl acetate (lab 1, 0.86), and amyl acetate (lab 1, 0.86). Desorption efficiencies ranged from 0.33 to 0.69 for acrylonitrile at both laboratories with all three sorbents and were 0.55 and 0.84 for acetone respectively with Pro-Tek and GASBADGE elements. Values obtained with concentrations equivalent to 0.25 and 0.50 TWA-TLV (ACGIH 1980) at laboratory 2 were about the same as those obtained at 0.05 TWA-TLV, which were subsequently used for calculations of concentration of organics in air.

Test atmosphere results obtained for the three sampling devices, after storage of elements and sections at 4^{0}C for 13 days, are summarized in TABLE II. Complete volatilization, no sorption on surfaces, and no losses from the chamber were assumed for the calculated (TABLE II) concentrations of organics. Air velocities

near the sampling devices were measured at <0.01 m/s (no fan) and about 0.2 m/s (fan), and the relative humidity and temperature were 50 ± 5% and 22 ± 1°C during the two tests. For some analyses which showed unusual peak area values, peak height measurements were used to check and sometimes to calculate the concentration of organics in air.

The precision of results from triplicate determinations by any one device was generally better than 10% RSD and was frequently better than 5% RSD for the test conducted with an air velocity of 0.2 m/s. Poor precision was found at laboratory 1 for 1,1,2-trichloroethane (24-41% RSD, all three devices) and amyl acetate (32% RSD, charcoal tube) and at laboratory 2 for dichloromethane (25% RSD), acrylonitrile (17% RSD), and hexane (26% RSD) with the GASBADGE in the test with air velocity of <0.01 m/s. At laboratory 1 and with air velocity of < 0.01 m/s, values obtained by means of the two passive monitoring devices were generally within ± 15% of the mean value for the two devices and GASBADGE results were generally of lower value than those for the Pro-Tek device. However, at laboratory 2 the two sets of values often ranged more than ± 15% about the mean value, and GASBADGE values were less than 80% of Pro-Tek values for 10 compounds. Corresponding values obtained at the two laboratories were within ± 15% of their mean value, except for acrylonitrile (GASBADGE, ± 20%), ethyl acetate (Pro-Tek, ± 23%; GASBADGE, ± 28%), and 1,1,2-trichloroethane (GASBADGE, ± 20%). Pro-Tek results obtained at the two laboratories were similar in value but GASBADGE values from laboratory 2 were generally lower than those from laboratory 1. Values obtained at laboratory 1 with the charcoal tube were generally more than 20% greater than the corresponding values obtained with the passive monitoring devices at <0.01 m/s air velocity. Methyl ethyl ketone, ethyl acetate, and amyl acetate values obtained with the Pro-Tek device were notable exceptions. Low readings, as compared to values obtained by the charcoal tube technique, can be expected (TOMPKINS & GOLDSMITH 1977) for the passive monitoring devices, due to "starvation" at the device face, when air velocity is less than 0.08 m/s. Concentration values obtained by means of the GASBADGE devices in a test with air velocity of about 0.2 m/s, or greater than the minimum velocity of 0.18 m/s recommended for the Pro-Tek device, are listed in TABLE II. Values obtained by the charcoal tube technique ranged from 79% to 103% of the calculated concentration (TABLE II), the "% recovery" roughly decreased with increasing boiling point for the compounds investigated, and concentration values were generally similar to those obtained with air velocity <0.01 m/s. Pro-Tek and GASBADGE values were ≥76% of the corresponding charcoal tube values, except for dichloromethane (Pro-Tek, 63%; GASBADGE, 18%) and chloroform (Pro-Tek, 62%; GASBADGE, 53%). GASBADGE values were, on the average, about 8% lower than the Pro-Tek values.

TABLE II. Concentration[a] (ppm) of Compounds in Test Atmosphere

Compound	Calculated[b]	Three methods		GASBADGE		
		Fan Lab1	No fan Lab1	Fan Lab1	No fan Lab1	No fan Lab2
Dichloromethane	9.0	5.6	5.4	1.7	3.6	2.9
Acrylonitrile	14.2	12.3	11.1	11.5	6.2	4.1
Chloroform	6.4	4.7	4.3	3.5	2.9	N[c]
Methyl ethyl ketone	10.6	10.2	6.3	8.8	5.0	3.9
1,1,1-Trichloroethane	5.7	6.3	4.3	6.4	3.6	3.0
Ethyl acetate	8.6	7.7	7.2	6.7	6.2	3.5
1,1,2-Trichloroethane	5.7	4.7	3.3	4.2	2.7	1.8
Benzene	9.7	8.1	6.5	7.8	5.0	4.2
Hexane	8.8	7.8	6.8	7.6	6.7	7.4
Tetrachloroethylene	4.6	3.7	2.9	3.9	2.2	1.7
Toluene	8.3	7.1	5.6	6.9	4.2	3.1
Amyl acetate	5.8	4.4	2.9	3.9	2.1	2.4
Octane	6.7	5.3	4.6	4.9	3.1	2.9
o- & p-Xylenes	14.4	11.9	9.2	11.6	6.7	6.4

[a] Mean value from three determinations (devices). See text. [b] Calculated for 500 uL of standards mixture in 1.01 m^3. [c] Not determined.

The mean of values obtained by all three methods for each test Concentration values obtained by means of the GASBADGE devices are also listed for each component in TABLE II. Three method precision was better than 15% RSD for all compounds except dichloromethane (68% RSD) and chloroform (35% RSD) when the air velocity was 0.2 m/s, but was worse than 15% RSD for all compounds except ethyl acetate (13% RSD) when the velocity was <0.01 m/s. Values obtained at <0.01 m/s were significantly lower than those obtained with air velocity at 0.2 m/s, largely due to the low readings obtained with the passive monitoring devices, as mentioned earlier.

Experimentally determined Pro-Tek sampling rates for dichloromethane, acrylonitrile, ethyl acetate, and amyl acetate, and GASBADGE dosimeter sampling constants for the same four compounds and chloroform, methyl ethyl ketone, 1,1,2-trichloroethane, and octane were not available. The available values (ABCOR 1978, DUPONT 1980), which were calculated from diffusion coefficients and device parameters, may be inaccurate and their use in concentration calculations may provide results which are slightly in error. Some discrepancies found for the concentration values in TABLE II may be due to the lack of an adequate technique (DOMMER & MELCHER 1978, EVANS & HORSTMAN 1981) for accurate determination of desorption efficiency values. Sorbent loading capacity can probably be discounted as a factor influencing the accurate determination of organics in these tests since the total organic load on the

charcoal elements and 100 mg sections never exceeded 2.5 mg. No organics were detected in the backup charcoal sections or for any of the blank determinations.

Offices in a variety of businesses (e.g. insurance, real estate, architectural, accounting, engineering, consulting, and legal firms) situated within the Ottawa urban core, as well as in the suburbs (3 offices) were surveyed. Information on test site particulars included building age (1 to 25 yr), total number of storeys (2 to 20), test site storey (1 to 11), and ventilation type. Ventilation systems were categorized as: "basically open" (8 offices) - no central air conditioning and windows in offices could be opened; "basically sealed" (6 offices) - central air conditioning but windows in some areas of building could be opened; and "completely sealed" (16 offices) - air conditioning only for ventilation. Several potential sources of organics, as determined from questionnaire responses, were present in each office for the majority of offices.

Potential sources of organics and the number of offices where they were reported were tobacco smoke (25), typewriter fluids (18), ink (14), glues-adhesives-thinners (10), copy machine chemicals (16), cosmetics (20), cleaning solvents (13), alcohol (1), paints-coloring material (2), aerosols-deodorizers (6), gasoline-naphtha-hexane-acetone (1), and tile caulking (1). The air temperature and relative humidity, which respectively ranged from 21^{o}C to 28^{o}C and 12% to 59% for all the offices, were considered to be such as to permit reliable use of the monitoring devices. Sampling by means of GASBADGE and Pro-Tek passive devices proved to be a facile technique for determination of organics in air and allowed minimum disruption of office routines.

Detection limits for 6 h exposures of the activated monitoring devices were determined from the available experimental data and other technical information (ABCOR 1978, DUPONT 1980). For the 51 compounds listed in TABLE I, except ethanol and methyl acetate (about 1 ppm), the detection limits were approximately 0.2 ppm. As shown in TABLE III, dichloromethane, tetrachloroethylene, and toluene were identified and detected at levels >0.2 ppm in the air of 8 of the surveyed offices. Unidentified, peaks were found in chromatograms for 6 offices including offices no. 3,4,5, and 7 (TABLE III). Levels of all identified compounds were well below their respective ACGIH, 8 h TWA-TLV values (ACGIH 1980).

Since the sparse data (TABLE III) generally included values near the detection limits, statistical comparison (HICKEY & BISHOP 1981) of the survey results was not considered meaningful. The relative merits of the monitoring devices and personal and area monitoring could not be evaluated for field conditions. No evident correlation could be found between type of business, building identity, age, and ventilation type, potential sources of organics, and the levels of organics in the office air. However, the possible sources of identified air contaminants were

usually evident, e.g. the use of copy machine chemicals and the occurrence of tetrachloroethylene.

TABLE III. Offices with Organics in Air Levels ≥ 0.2 ppm.

Dichloromethane (ppm)[a]	Tetrachloroethylene (ppm)[a]	Toluene (ppm)[a]
1[b] - 0.7	4 - 1.1(1.4)	7[b] - 0.2
2 - 0.7 (0.8)	5 - 1.0	8[b] - 0.3
- 0.4 (0.5)	6[b] - 1.1	- 0.3
- 0.4[c](0.6)[c]	- 1.0	- 0.3[c]
3 - (0.4)	- 1.1[c]	
4 - 5.9 (8.2)		

[a] Values in brackets for matching Pro-Tek badges.
[b] Only GASBADGE devices used here. [c] Area monitor.

ACKNOWLEDGEMENTS. Review of the manuscript by J.R. Harrison and V. Paramasigamani and typing by J. Ireland is gratefully acknowledged.

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Accepted March 2, 1983