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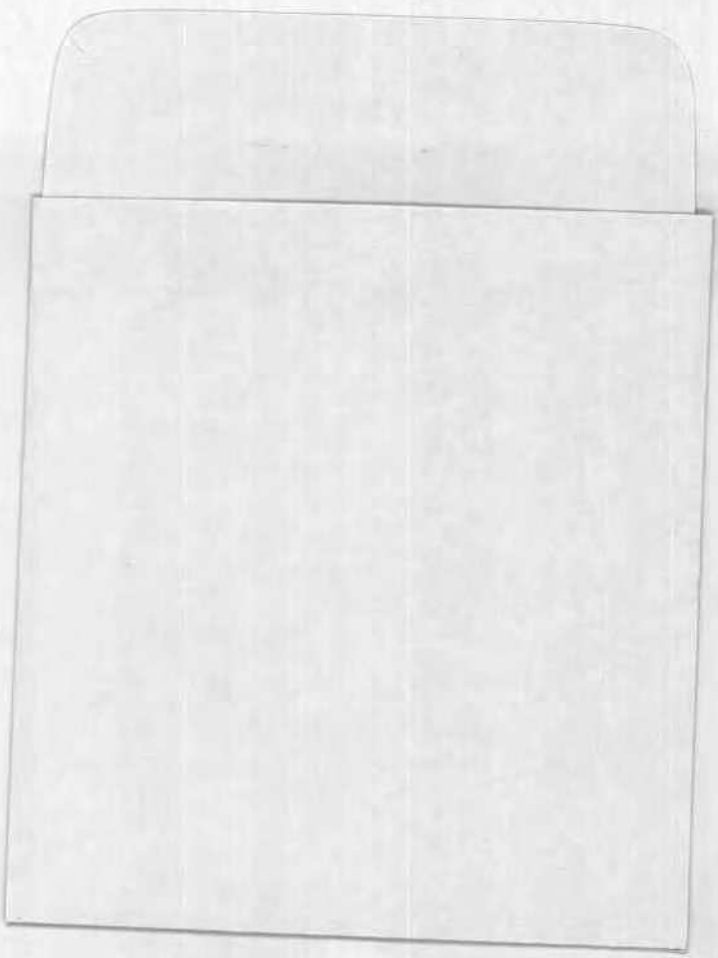
RÉSUMÉ

On a étudié, surtout à l'aide de tubes de sorption et de CG/SM, la concentration globale et les profils des produits organiques volatiles contenus dans l'air de plusieurs immeubles à bureaux comprenant des bibliothèques. On a constaté que les vapeurs d'échappement provenant des photocopieuses à procédé humide étaient à l'origine d'un grand nombre des produits organiques volatiles contenus dans l'air des locaux.



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Short Communication

WET PROCESS COPYING MACHINES: A SOURCE OF VOLATILE ORGANIC COMPOUND EMISSIONS IN BUILDINGS

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Abstract—The total volatile organic compounds and profiles of volatile organic compounds of indoor air in several office buildings with libraries were studied, mainly using sorption tubes and GC-MS. Exhaust vapors from wet-process-type copying machines proved to be a major source of the volatile organic components of the indoor air.

Keywords—Indoor air Libraries GC-MS Sorption tubes

INTRODUCTION

Indoor air quality studies were performed in four buildings, referred to as Building Nos. 1 to 4. The studies involved (a) measurement of total volatile organic compounds (TVOC), (b) identification of volatile organic compounds (VOC) with an atmospheric pressure chemical ionization tandem mass spectrometer (APCI/MS/MS), and (c) determination of the profiles of VOC by gas chromatography/mass spectrometry (GC-MS).

EXPERIMENTAL METHODS

Air sampling

Air was sampled using two procedures. The first was bag sampling: room air was taken directly into a 20-liter Teflon bag for APCI/MS/MS analysis. The second method used a sorption tube (20 cm long, 4 mm i.d. glass tube) packed in series with glass beads, Tenax-GC, and Ambersorb XE-340. Volumes of sampled air varied from 10 liters to 1 ml, depending on the expected concentrations of organic compounds in the air. The general sampling rate was 250 ml/min.

Analysis

The SCIEX model TAGA 6000 allowed APCI/MS/MS analysis in real time without having to concentrate the organic compounds in air, with the exception of hydrocarbons, halogenated hydrocarbons and formaldehyde. The details of the use of this instrument are described elsewhere [1].

For GC-MS analysis, the organic compounds collected in the sorption tube were thermally released at 220°C under a helium current, using an Envirochem Unacon Model 810 desorbing unit. Effluents from the sorption tube were split and about 88% of the effluent was injected into a Hewlett-Packard Model 5996 GC-MS. A methylsilicone bonded-phase capillary column (50 m × 0.32 mm i.d.) was used for the GC separation. The oven temperature was programmed from −50 to 250°C, increasing at a rate of 10°C/min.

Components of the GC effluent were identified by MS using a spectra library and a search program, both of which were supplied by the manufacturer of the instrument. The library consists of over 70,000 spectra, including the NIH/EPA/Mass Spectra Data Base (NBS Library) and the Registry of Mass Spectra Data (Wiley Library). In this study, however, determination of VOC profiles, rather than the identification of each

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Some commercial equipment is identified in this article to adequately specify 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.

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component, was the main purpose of the GC-MS analysis.

Although the GC-MS detects all types of compounds, it has been noted that hydrocarbons of carbon number 1 and 2 break through the sorption tube; they were not included in the analysis.

TVOC were determined by flame ionization detection (FID). The 8% portion of the split effluent went into the FID; the single peak on the FID trace was integrated using a Hewlett-Packard Model 3392A integrator. For the calibration of the FID, various volumes of a standard gas (782 ppm *n*-hexane in helium) were drawn into sorption tubes and analyzed as described for the samples. The concentration of standard gas was checked by the diffusion tube method [2] using a VICI Metronics Model 340 Dynacalibrator. Formaldehyde was not detectable by the FID; thus it was not included in the TVOC.

Emissions from printed materials

To test whether printed materials were absorbing and re-emitting VOC, about 20 kg of books, journals and newspapers taken from Building No. 1 were placed in a closed polyvinyl chloride and polymethyl methacrylate box ($0.7 \times 0.8 \times 1.0$ m). After 24 h, the headspace gas was sampled and analyzed by GC-MS as described above.

RESULTS AND DISCUSSION

APCI/MS/MS analysis

Only insignificant quantities of organic compounds were detected by APCI/MS/MS analysis. This meant that any VOC detected could be considered to be essentially hydrocarbons or halogenated hydrocarbons (they were hydrocarbons, as shown later).

TVOC

The TVOC results for several locations in four buildings are given in Table 1. Amounts present in Building No. 1 were similar to those in Building No. 2. The relatively low TVOC result in Building No. 3 may be due to the much higher air supply rate there. Molhave [3] postulated that irritation of mucous membranes by VOC of the solvent type is possible in a concentration threshold range of 0.16 to 2.0 mg/m^3 and is probable if concentrations exceed 2 mg/m^3.

GC-MS analysis

The VOC profiles from all locations in Building No. 1 (only 2 of 20 measurements are shown in Fig. 1a and b), in the library of Building No. 2 (Fig. 1c) and in the library of Building No. 3 (Fig. 1d), as obtained by GC-MS, were similar. These profiles were distinguishable from those previously obtained in houses and offices by characteristic branched-alkane groups containing 8 to 12 carbon atoms. The exact structures of most of the branched alkanes were not determined, but the major component was 2,2,4-trimethylheptane.

Exhaust from copying machines

There are six units of Model A photocopying machines in a sixth-floor office in Building No. 1; a Model B of the same make and a Model C printer of another make are located in Building No. 2. Direct exhaust from a Model A machine in the sixth-floor office exhibited the same VOC profile (Fig. 1e) as that in the air of the other parts of the building, but with a concentration 2,000 times higher (Table 1, No. 8). The headspace gas from the copying-machine fluid container had the same profile at a concentration about 50,000 times higher (Table 1, No. 9). It is estimated from the area under the peaks in the chromatogram (Fig. 1b) that about 99% of the TVOC found in the sixth-floor office in Building No. 1 originated in the copying machines' exhaust vapors.

The concentration of VOC in the exhaust from the Model D copying machine in Building No. 4 was 3,000 times lower than in the Model A copier exhaust (Table 1, No. 10). Model D copiers use a dry process, while Models A, B, and C use a wet process. In the wet process, the copying paper is moistened with a crude isodecane solvent (average formula, $C_{10}H_{22}$) and isodecane vapors are given off when the paper is dried [4].

To confirm that the main components in the air of Building No. 1 and the copying machine ex-

Table 1. Total volatile organic compounds (TVOC)

No.	Sample location	TVOC (mg/m^3)
1	Bldg. No. 3, library	0.13
2	Bldg. No. 2, library	1.58
3	Bldg. No. 1, 1F SE	1.77
4	Bldg. No. 1, 1F-GF stairway	1.18
5	Bldg. No. 1, GF SE	2.36
6	Bldg. No. 1, 1F NW	0.90
7	Bldg. No. 1, 6F office	64.0
8	Bldg. No. 1, 6F Model A copier exhaust	4,150
9	Model A copier liquid	107,000
10	Bldg. No. 4, 2F Model D copier exhaust	1.42

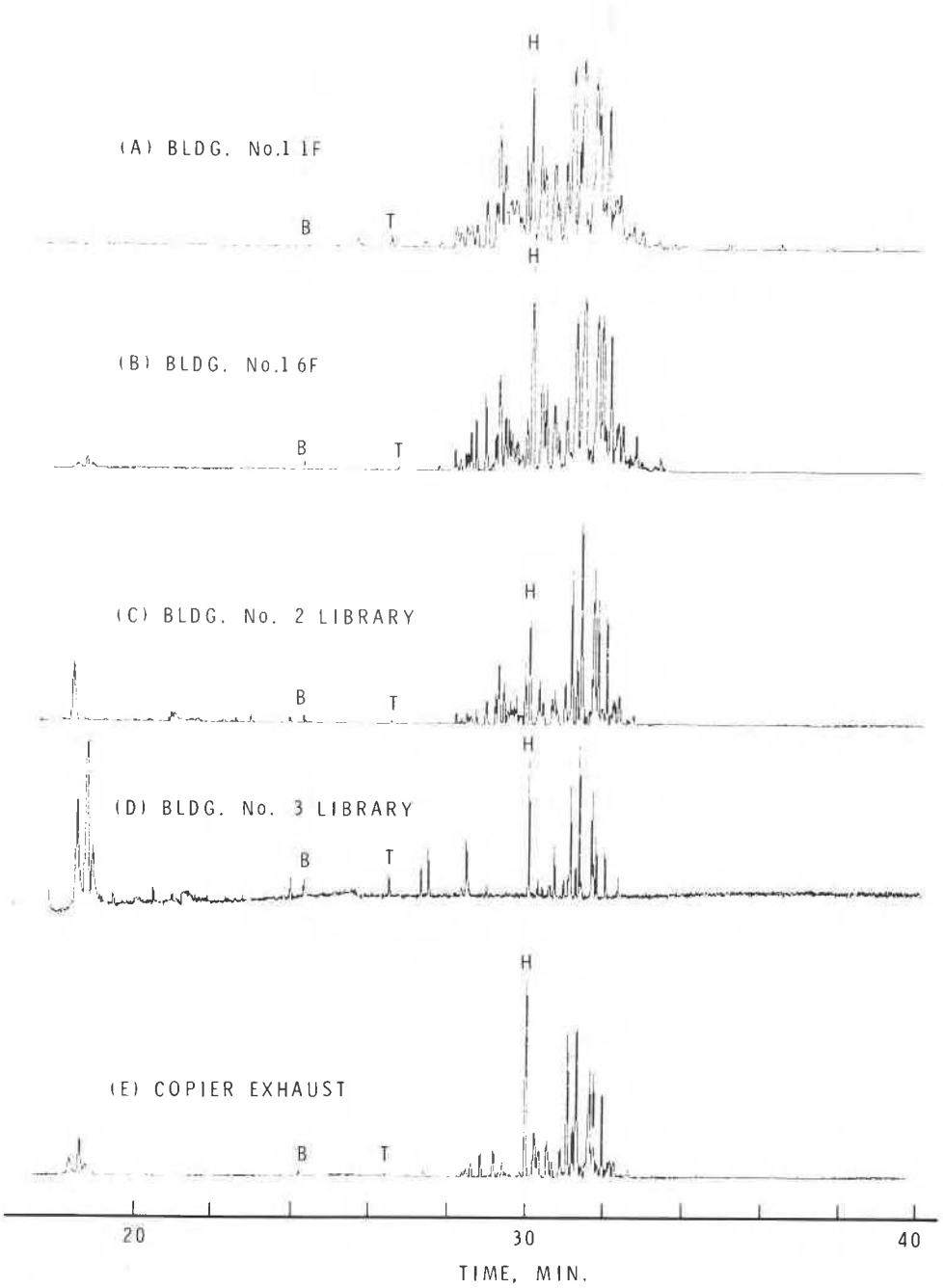

Fig. 1. GC-MS profiles of volatile organic compounds in air. B, benzene; T, toluene; H, 2,4,4-trimethyl heptane.

haust were the same, single ion chromatograms (SIC) on major ions were studied. The SIC was a standard feature of the data system of the GC-MS. Single ions of mass-to-charge ratio detected on the MS (m/e = 43, 57, 71, 85, 99, 113, 127, 141) of copying machine exhaust and those of air in the building were compared. All of the major peaks in the SICs of exhaust were found in the SICs of building air.

The solvent from a photocopying machine using

a wet process has previously been reported to cause irritation of the eyes and skin among post office workers [5].

The VOC profiles shown in Figure 1 point to the usefulness of a recognized GC-MS fingerprint. The same profile was obtained before the present study following an indoor air quality complaint in an office that had been newly furnished. While the VOC source could not be established at that time, it is now evident that over 90% of the TVOC could have come from three copying machines situated within a 20-m radius of the office. In the air of Building No. 3, though the TVOC was low, copier exhaust accounted for 67% of the TVOC (Fig. 1d).

Emissions from printed materials

Copier exhaust fingerprints were present in the VOC emissions from newspapers and books taken from Building No. 1. In contrast, the fingerprint was absent in the emissions from newspapers taken from the newsstand and from books taken from Building No. 4.

It is considered most likely that copier exhaust VOC, which are absorbed on surfaces such as printed materials and upholstery, can subsequently be re-emitted over a period of time even when the VOC source is no longer present.

CONCLUSIONS

Exhaust vapors from photocopying machines using a wet process proved to be a major source of the volatile organic compounds in the indoor air in three of four buildings studied. The GC-MS profile of copier liquids can be used to identify copying machines as major sources of VOC in air.

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