Measurement of Indoor Air Emissions from Dry-Process Photocopy Machines

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ABSTRACT

Presently, no standard test method exists to evaluate the various emissions from office equipment (e.g., ozone, volatile organic compounds, inorganic gases, and particulates) so it is difficult to compare data from different studies.[1] As a result, the authors are developing a standardized guidance document for measuring indoor air emissions from office equipment. The ultimate goal is to apply the test method to better understand emissions from office equipment and to develop lower emitting machines. This paper provides background information on indoor air emissions from office equipment with an emphasis on dry-process photocopy machines. The test method is described in detail, along with the results of a study to evaluate the test method using four dry-process photocopy machines.

The results from this study indicate that the test method provides acceptable performance for characterizing emissions; that it can adequately identify differences in emissions between machines both in compounds emitted and their emission rates; and that it is capable of measuring both intra- and inter-machine variability in emissions. Challenges and complications were encountered in developing and implementing the test method. These included heat generation, which can cause large increases in chamber

temperature; finite paper supplies for photocopy machines, which limit test duration; varying power requirements that may require changes in chamber electrical supply; and remote starting of the machines, which is necessary to maintain chamber integrity.

Results show that dry-process photocopy machines can produce emissions of ozone and volatile organic compounds that can potentially have a significant impact on indoor air quality. For the four machines tested in this study, the compounds with the highest emission rates overall were ethylbenzene (28,000 µg/hour), *m,p*-xylenes (29,000 µg/hour), *o*-xylene (17,000 µg/hour), 2-ethyl-1-hexanol (14,000 µg/hour), and styrene (12,000 µg/hour). Although many of the same compounds tended to be detected in emissions from each of the four photocopiers, the relative contribution of individual compounds varied considerably between machines, with differences greater than an order of magnitude for some compounds.

INTRODUCTION

Indoor air emissions from office equipment and associated supplies include ozone, volatile organic compounds (VOCs), inorganic gases, and particulates.[1] According to the literature, specific emissions from photoimaging equipment include ammonia, benzaldehyde, benzene, butyl methacrylate, cyclotrisiloxanes, ethylbenzene, isopropanol, methylmethacrylate, nonanal, ozone, styrene, terpenes, toluene, trichloroethylene, 1,1,1-trichloroethane, xylenes, and zinc stearate combustion products.[2]

Indoor air emissions from office equipment may result from equipment operation, off-gassing from components, or episodic releases.

- Equipment operation. This may include both emissions from the use of supplies (e.g., toner and paper) and ozone emissions associated with the operation of electronic equipment. Emissions from operation may either remain fairly constant or increase between routine maintenance and as the equipment ages. For example, one study showed that ozone emissions from five photocopiers ranged from 16 to 131 µg/copy

before routine maintenance. Emissions were reduced to less than 1 to 4 µg/copy after maintenance.[1]

- Off-gassing from components. Residual organics can off-gas from any type of office equipment, even if the equipment does not use supplies (e.g., video display terminals). The source of these organics can be construction materials (e.g., plastic casings), components (e.g., cards used for circuit boards), or solvents used in manufacturing or cleaning the equipment. Emissions resulting from off-gassing decrease with time. One study of video display terminals showed that over 300 hours of "on time" is required before emissions decrease appreciably.[1] Higher temperatures will increase the rate of emission.

- Episodic releases. Catastrophic failure of a unit can result in episodic releases of organics due to venting of capacitors and/or charring of components.

Numerous studies have documented various adverse health effects from exposure to emissions from office equipment.[1] One study measured increased levels of ozone, formaldehyde, total VOCs, and particulates in a 6-hour chamber test with operating office equipment.[3] Thirty human subjects participating in the experiment had a significantly increased perception of headache; mucous membrane irritation; dryness in the eyes, nose, and throat; and dry and tight facial skin. Another study, conducted by the National Institute of Occupational Safety and Health (NIOSH), indicated that the use of a photocopier was significantly associated with reported symptoms.[4] Individuals in the study who complained of symptoms were 1.5 to 2.5 times as likely to have been exposed to photocopiers as those without complaints.

Although several studies have evaluated indoor air emissions from various types of office equipment,[1] the studies have not followed any standard method or protocol that would permit a reasonable comparison of the results from different studies. Additionally, current methods often focus on measuring high levels of emissions (i.e., those that would result in exposures that exceed occupational limits) and may not be sensitive enough to adequately identify emissions at the levels typically found in office environments.[1] Therefore, a test method is needed which will allow for comparison of results between different machines and manufacturers; will have the analytical sensitivity to allow identification of the range of pollutants emitted and their emission rates; will be applicable to all types of office equipment; will provide minimum performance standards while allowing for flexibility to accommodate different emission test facilities; and will be sufficiently rugged to help determine the root causes of emissions in order to ultimately develop lower-emitting equipment.

TEST METHOD

This section provides an overview of the test method developed as part of this project. The test method was developed based on the experience of researchers at Research Triangle Institute (RTI) and at EPA's Air Pollution Prevention and Control Division (APPCD). The draft method was also reviewed by the industry technical advisors participating in this project. The chamber, the sample collection and analysis method, the actual test method procedure, and data analysis are described. The method emphasizes emissions of VOCs, aldehydes/ketones, ozone, and particulates.

The description of the test method below serves two purposes: 1) It accurately presents the specific test conditions followed for this study, and 2) it provides relevant information that can be used by other researchers. The description of the test method is followed by a discussion of emissions tests results from four dry-process photocopiers evaluated as part of this study.

Test Chamber

The test method developed for this study uses flow-through dynamic chambers because they are generally applicable to all types of equipment and generally mimic typical use conditions found in an office. The major components are the test chamber, the air mixing system, the environmental control systems, and the sample collection and analysis equipment. Minimum chamber performance requirements are presented below, and specific information on the chamber facilities and test conditions used for this study is in Table 1.

Chamber Construction. The interior surfaces of the chamber must be nonadsorbent and chemically inert to minimize the potential for interior walls to act as either sinks or sources of chemical pollutants. Inert surfaces such as stainless steel or aluminum are recommended. Other materials (e.g., Tedlar) may also be used. All joints should be permanently sealed (except required openings) to minimize the potential for leakage. Seals and sealant must be nonadsorbent, with minimal use of caulks and adhesives that may emit or adsorb VOCs. An airtight access door, inlet and outlet ports for air flow, and temperature and humidity probes are also required.

The chamber's linear dimensions should be a minimum of 1.4 times the dimensions of the equipment tested; e.g., the minimum size chamber for a machine measuring 1.5 m by 1 m by 0.5 m is 2.1 m by 1.4 m by 0.7 m. The value of 1.4 was selected based on the manufacturers' prior experience in chamber testing. Its primary basis is to allow for adequate space for servicing equipment in the chamber, while also allowing for air movement.

The chamber should operate under positive pressure to eliminate infiltration of contaminants. The air intake and exhaust ports should be on different walls of the chamber and at different elevations; alternative designs are allowed if it can be shown that the chamber air is well-mixed.

Air Mixing System. Mixing ensures that equipment emissions are accurately measured. Low-speed mixing fans or

Table 1. Description of large chamber environmental test chamber at RTI and conditions for chamber testing.

Parameter	Description
Size	800 cu ft (22.7 m³) [10 x 10 x 8 ft (3.05 x 3.05 x 2.44 m)]
Construction Materials	Ducts: Aluminum Ceiling/Walls: Aluminum Floor: Stainless Steel Gaskets: Viton
Air Supply System	Outdoor air passed through particulate filters, then through Carasorb 200 filters for organics removal, followed by high efficiency particulate air (HEPA) filtration and a final charcoal filter
Sampling Ports	1/4-in. (0.645 cm) stainless steel Swagelok adaptable to meet other requirements
Measurement Systems	Temperature/Humidity-General Eastman Model 850 Air Flow - Carrier Comfort Network Distributed Controller Data Acquisition - 386 PC
Temperature Control Test Method	65 to 94 °F ± 2 °F (18 °C to 35 °C ± 1 °C) 26 °C to 31 °C
Humidity Control Test Method	40% to 70% RH, ± 5% 30% to 35% RH
Air Exchange Rate Test Method	0.2 air change/hour to 2 air changes/minute 2.0 ± 0.2 h⁻¹
Copier Operation Time	20 to 40 minutes
Sample Collection Time	140 to 160 minutes
Loading (L)	1 Copier

multiport inlet and outlet diffusers should be used. Motors for mixing fans should be located outside the chamber to ensure that contaminants (e.g., from lubricants and plasticizers) are not introduced into the chamber. The American Society for Testing and Materials (ASTM) D5116-90, "Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products"[5] can be used to characterize the completeness of mixing in the chamber.

Environmental Control Systems. Controls are required to maintain a constant temperature and relative humidity (RH), to generate clean air for chamber tests, and to provide a constant air exchange rate.

Chamber temperature should be maintained at 26 °C to 31 °C by conditioning the inlet air. This temperature range is a practical compromise between typical chamber conditions (e.g., 23 °C) and temperatures that can be achieved when equipment that has a high thermal load is tested. Initial testing for this project indicated that photocopiers can produce large amounts of heat, up to 24,000 Btu/hr (25,322 kJ/hr), and as a result, it may be difficult to maintain temperatures below 26 °C.

The background chamber air concentration must be maintained at or below detection limits for the target analyses by using clean inlet air. Organics and ozone can be removed from the chamber supply air using charcoal filters, oxidizing filters, and catalytic oxidizers; high-efficiency particulate air (HEPA) filters can effectively remove suspended aerosols.

Air flow should be automatically monitored and controlled by electronic mass flow controllers or manual flow control. An air exchange rate of 2.0 ± 15% air changes per hour (ACH) was chosen for this method because it is a reasonable approximation of normal indoor conditions (approximately 1 ACH) and also addresses the need to dissipate heat that may be generated by equipment operation while still maintaining a temperature between 26 °C and 31 °C.

RH within the chamber should be maintained between 30% and 35%. Initial experiments targeted 50% RH; however, at the high end of the temperature range (31 °C), it was not possible to meet 50% RH. It was also anticipated that the amount of water needed to maintain 50% RH in the chamber might cause problems with water collection on the sorbent tubes during VOC analysis. A RH of 35% at 31 °C represents a mass of water equivalent to 50% RH at 23 °C.

Sample Collection and Analysis

The chamber design and operation should allow for continuous equipment operation and for sampling of chamber air without violating chamber integrity. All sampling systems that contact chamber air prior to collection or measurement should be constructed of inert materials. For example, ozone must contact only Teflon and glass surfaces. Particle collectors and counters should be located near the exhaust port within the chamber. External particle counters must be connected through sample lines designed to minimize losses of particles up to10 μm in diameter.

Depending on the type of equipment being tested, chamber air concentrations of certain compounds may be relatively low, requiring larger sample volumes and the use of integrating sample collection media (e.g., adsorbent). The

recovery efficiency must be determined for collection and analysis of representative chemical constituents, and background concentration recoveries must meet designated performance standards. Target detection limits for chamber air concentrations are set at 0.25 to 1.5 $\mu g/m^3$ (typical concentration background for individual VOCs in indoor air), levels of concern for specific health effects, odor thresholds, or 1% of the threshold limit value (TLV), whichever is smaller. For total VOCs, a target detection limit of 5 $\mu g/m^3$ has been set. The specific methods used for this project are summarized in Table 2. Alternative sample collection and analysis methods are acceptable if they can be shown to achieve similar performance.

Test Procedure

To ensure a well-defined test and reproducible and comparable results, consistency in chamber preparation, test duration, and equipment operation should be maintained. Each of these is described below. Furthermore, to enhance comparability of data between chambers, recovery tests releasing known quantities of standard gases should be conducted.

Chamber Preparation. The chamber should be cleaned prior to testing. A recovery efficiency test for gas-phase contaminants (e.g., VOCs, aldehydes, and ozone) should be conducted in the empty chamber to determine the potential

Table 2. Methods for measuring chamber air concentrations of target analytes.

Analytes	Method
VOCs	VOCs in air samples (1 to 8 L) collected on multisorbent tubes. Tubes analyzed by gas chromatography/mass spectrometry. Screening and quantitation samples collected and analyzed. Screening samples used to identify target VOCs. Quantitation samples used to measure air concentrations of target VOCs using a multipoint calibration.
Aldehydes/ketones	Aldehydes/ketones in air samples (36 L) collected on 2,4-dinitrophenylhydrazine (DNPH)-coated silica gel cartridges. Cartridges were solvent desorbed with acetonitrile. Extract analyzed by high performance liquid chromatography (HPLC). Concentrations in sample extracts measured using a multipoint calibration.
Ozone	Continuous monitoring of chamber air concentrations using a DASIBI model 1003-AH ozone monitor.
Particles	Continuous monitoring of chamber air particle concentrations using a LAS-X optical particle counter.

for wall effects (where a chemical may adhere to chamber walls, gaskets, or other chamber materials). This test should be conducted by spiking inlet air with a known amount of a contaminant (e.g., minimum of 10 times the detection limit) and measuring the amount recovered.

Background levels of target pollutants in the chamber air should be measured before each test and should be below the detection limits established for the individual pollutants. Chamber air should then be measured with the equipment idling (i.e., powered but not operating) to obtain data on off-gassing. This measurement should be taken at least 2 hours (i.e., equivalent of four air changes) after the equipment is placed in the chamber to ensure that equilibrium conditions have been reached.

Test Duration. The test should be of sufficient duration to ensure that chamber equilibrium is reached or that total emissions are measured. In general, four air changes are required to replace 98% of the air in the chamber used for this project, since it is a single-pass system. Based on the specified ACH of 2.0, a 2-hour test is required for this chamber. Three alternative approaches can be used:

- The equipment operates for 2 hours continuously, at which time sampling could occur; in the absence of wall effects, the chamber air concentration is assumed to be in equilibrium.
- The equipment operates for a defined period of time, collecting an integrated sample from the start of operation until 2 hours (i.e., four air changes) after the equipment is turned off. In the absence of wall effects, this sample should represent about 98% of total emissions during operation for the chamber used in this study.
- Short-term periodic samples are taken throughout the period of operation. This approach should be used when information on the time course of emissions is required. This option is useful to determine how emissions change with time of operation.

Some types of office equipment, such as photocopy machines and printers, can operate unattended only for a limited period of time due to a finite paper supply. If the equipment cannot operate continuously for the 2 hours required for the chamber to reach equilibrium, plus the time required to collect a sample, then one of the following approaches must be used:

- Multiple machines must operate sequentially so that operation is continuous for the time period required (6 hours).
- An integrated sample must be taken from the start of operation until 2 hours (four air changes) after the cessation of operation.

For the machines evaluated in this study, 2,000 copies were printed for each test, and an integrated sample was collected from the start of operation until 2 hours (i.e., four

air changes) after the paper supply was exhausted. The paper supply of 2,000 sheets was exhausted after 20 to 40 minutes, resulting in a total sample collection time of 140 to 160 minutes.

Equipment Operation. The equipment should be installed and thoroughly tested by an experienced photocopy technician prior to beginning the test. For this study, a service representative from each manufacturer installed and checked the photocopier in the chamber prior to testing. The toner recommended by the individual manufacturers was used for each test, and the same type of paper—20% recycled materials—was used for all testing.

To evaluate off-gassing, equipment should be tested while idling (i.e., power on but not operating) and at full maximum operation. For image processing machines (i.e., copiers and printers), a standard image has been prepared to represent a typical maximum image to define worst-case emissions and exposure. For monochromatic machines, the standard image represents about 15% coverage (i.e., worst case).

Chamber Evaluation (Recovery Tests). For this study, selected VOCs, formaldehyde, and ozone were introduced into the chamber at known rates. Procedures for generating and introducing these chemicals into the chamber air are outlined in Table 3. Chamber air samples were then collected and analyzed using procedures identical to those used during the emission tests with photocopiers (Table 2).

Table 3. Methods for generating standards with known emissions.

Chemical Class	Method
VOCs	Cylinder containing toluene and chloroform (~60 mg) prepared
	· 10 L volume metered into chamber at a rate of 1.0 L/min. Samples collected over 130-minute period.
	· 8 L volume metered into chamber at a rate of 0.2 L/min over 40 minutes. Time point samples collected for T = 0-10, 10-20, 20-30, 30-45, 45-60, 60-75, 75-90, 90-105, 105-120, and 120-160 minutes.
Aldehydes/ketones	Aqueous solution of formaldehyde (~53 mg/mL) delivered to chamber with HPLC pump, vaporized by passing through 350 °C heated tubing at rate of 2.1 mL/min for 30 minutes, samples collected over a 150-minute period.
Ozone	Generator producing ~90 ppm ozone at 1 L/min attached to chamber for 120 minutes. Monitored increase and decrease of chamber concentration.

Sample Collection. For VOCs and aldehydes/ketones, chamber air samples are collected and then analyzed for the target chemicals. A chamber air sample is collected first, prior to placing the copier in the chamber, to determine background levels in the chamber. A second chamber air sample is collected after the copier is placed in the chamber in the idle mode. This sample is collected after the copier reaches equilibrium in the chamber for a minimum of four air changes and provides data on the off-gassing of chemicals in the idle mode. Finally, a third chamber air sample is collected from the time the copier starts printing until 2 hours (four air changes) after printing is completed. This sample provides data on the average time-integrated chamber air concentration over the test period (140 to 160 minutes for the machines in this study).

Data Analysis

Chamber air concentrations for individual pollutants are calculated as follows: 1) Normalized mass may be adjusted for system background and chamber background, and 2) Adjusted mass is divided by the sample volume to generate chamber air concentration.

Recovery Tests. The measured amount of pollutant emitted during each test was calculated as:

$$E_m = C_c * V_C * A_c * T_s \qquad (1)$$

where,

E_m	=	the measured amount of target pollutant emitted during each test in µg
C_c	=	the measured chamber air concentration in mg/m³
V_C	=	the chamber volume in m³
A_c	=	the air exchange rate in h⁻¹
T_s	=	the sample collection time in h

Percent recovery of the emitted pollutant was used to evaluate accuracy of the emission test method. Percent recovery (%R) was calculated as:

$$\%R = E_{am}/E_{as} * 100 \qquad (2)$$

where E_{am} is the measured amount emitted in µg and E_{as} is the amount that was actually emitted in µg during the test.

Emission Factor Calculation. Time integrated emission rates (ERs) were calculated from the resulting chamber air concentration data as:

$$ER_i = (C_i - C_b) * V_C * A_c \qquad (3)$$

where,

ER_i	=	emission rate in the idle mode in µg/h.
C_i	=	chamber air concentration in the idle mode in µg/m³

C_b = background chamber air concentration in µg/m³

V_C = chamber volume in m³

A_c = chamber air exchange rate in h⁻¹

and

$$ER_c = [(C_p - C_i) * V_C * A_c * T_c] / (T_p * n) \qquad (4)$$

where,

ER_c = emission rate during printing in µg/h • copier

C_p = time-integrated chamber air concentration during printing in µg/m³

T_p = time the copier was printing in h

n = number of copiers in chamber

For ozone, chamber air concentrations were measured over the test period using real time instruments. Here, these chemicals emission rates were calculated as:

$$Er_o = (C_c * A_c * V_C)/1 - e^{-AcTp} \qquad (5)$$

where,

Er_o = emission rate for ozone in µg/h • copier

C_c = equilibrium chamber air concentration in µg/m³

RESULTS AND DISCUSSION

A recovery study was conducted as a first step in order to evaluate the accuracy and precision of the emission rate measurements. The test method was then applied to collect data from four dry-process photocopy machines.

Chamber Evaluation

Recovery tests using integrated samples collected over the test period were conducted in triplicate for VOCs, toluene, formaldehyde, and ozone. Precision of the emission rate measurement was evaluated as percent relative standard deviation (%RSD) of the replicate tests. Results of the VOC recovery tests are summarized in Table 4. Results show acceptable precision and performance. Furthermore, the increase and decay curves for ozone within the chamber matched, indicating negligible wall effects.

Photocopier Emission Test Results

Mid-range photocopiers (30 to 135 copies per minute) were selected for this study because of their prevalence in the office environment and because

of their emissions of ozone, VOCs, inorganic gases, and particulates. The mean copy speed for mid-range machines is 59 copies per minute, and an effort was made to select machines from different manufacturers in the range of 40 to 80 copies per minute as representative of most mid-range photocopiers.[6] The basic characteristics of the four photocopiers tested in this study are summarized in Table 5.

Three experimental objectives were defined for this phase of testing:

1. To evaluate the precision of the emission rate measurements for one copier in the idle and full operation modes using a fixed set of operating conditions.
2. To evaluate the variability of emission rate measurements between copiers with different characteristics.
3. To evaluate the practical aspects of test method implementation.

Precision of Emission Rate Measurements. Precision of the emission rate measurements in the idle and print modes was evaluated by conducting triplicate tests on copier 1 and calculating the %RSD. Results are provided in Table 6 for the average emission rate measurements and their %RSD for the triplicate tests in both the idle and the print modes. In general,

Table 4. Chamber recovery test results.

	Measured emission (µg)				Recovery	
	Test 1	Test 2	Test 3	Amount Emitted (µg)	Mean %	% RSD
Chloroform	2662	2890	2569	3000	91	6.2
Toluene	2408	2532	2468	2100	118	2.1
Formaldehyde	2920	2946	3034	3400	88	2.0
Ozone (peak conc.)	13,400	13,200	11,200	17,600[a]	72	-

[a] Dräger tube measurement; accuracy of measurement is unknown.

Table 5. Characteristics/features of photocopiers tested.

Copier ID	1	2	3	4
Toner Type[a]	dry powder/ dual component	dry powder/ dual component	dry powder/ mono component	dry powder/ dual component
Development[b]	magnetic brush	magnetic brush	magnetic roller	magnetic brush
Fusing[c]	heat, pressure	heat, pressure	hot roller	heat, pressure
Photoconductor[d]	organic drum	organic belt	amorphous silica drum	organic drum
Copier Condition	used, ~50,000 copies	new, <100 copies	new, <100 copies	used, ~76,000 copies

[a] Dual-component toner consists of toner and a carrier. Monocomponent toner consists of toner alone, which is mainly resin and some magnetic material.
[b] A magnetic brush is used in dual component systems where the carrier and toner are oppositely charged. A magnetic roller is used in monocomponent systems to attract the charged particles.
[c] Fusing is the process in which the toner is permanently bound to the paper.
[d] The photoconductive drum or belt is typically coated with selenium, amorphous silica, organic dyes and pigments, or zinc oxide.

there is excellent precision (%RSD < 10%) for the emission rate measurements in the print mode. In the idle mode, where measured emission rates had much lower values, the %RSD tended to be higher.

Between Copier Variability of Emission Rate Measurements. The test method was then applied to measure emission rates for both idle and operation modes for four dry-process photocopiers. The results are expressed in micrograms/hour in Table 7.

As one might expect, measured emission rates were much lower in the idle mode than in the operating mode for all four machines. This indicates that the emissions from operation are much greater than emissions from off-gassing.

In general, the same compounds were detected for each of the four photocopiers. However, the relative contribution of individual compounds varied considerably between machines, with differences greater than an order of magnitude for some compounds. For copier 1, emission rates were greatest for ethylbenzene, xylenes, styrene, undecane, and acetone. Emission rates for copier 2 were greatest for styrene, benzaldehyde, 2-ethyl-1-hexanol, and *n*-nonanal. For copier 3, compounds with the greatest emission rates were

ethylbenzene, xylenes, styrene, propylbenzene, 2-ethyl-1-hexanol, *n*-nonanal, and formaldehyde. Finally, emission rates for copier 4 were greatest for *n*-nonanal, formaldehyde, and acetone. The compounds with the highest emission rates overall—but not necessarily from the same machine—were ethylbenzene (28,000 µg/hour), *m,p*-xylenes (29,000 µg/hour), *o*-xylene (17,000 µg/hour), 2-ethyl-1-hexanol (14,000 µg/hour), and styrene (12,000 µg/hour).

Ozone emissions were 3,000, 1,300, 4,700, and 7,900 µg/hour for machines 1 through 4, respectively. Limited particulate data were collected for two of the four machines tested. Results showed that operation of one of the machines increased particulate levels to 30 times chamber background levels for particles smaller than 2 µm in diameter.

CONCLUSIONS

Results of this study have provided valuable information on the performance of the test method and on emission characteristics of selected dry-process photocopiers.

1. The large chamber test method developed as part of this project provided acceptable performance for characterizing emissions from dry-process photocopy machines. Percent recovery for calculated emission rates for standard materials emitted into the chamber at known rates was greater than 85%. Precision of replicate tests using both standard emitters and photocopiers was good. In general, precision was much better for the emission rate measurements in the print mode, than in the idle mode, where measured emission rates had much lower values.

2. A standard test method for measuring indoor air emissions from office equipment can present numerous challenges and complications. Specific complications identified during this study include:
   - Heat generation. Depending on the machine, heat generation in the chamber may be a problem. As a result, the test method developed as part of this project specifies a temperature range of 28.5 ± 2.5 °C and an air exchange rate of two changes per hour.
   - Limited paper supply. A finite paper supply for copy machines limits the duration of the test. For this study, a paper supply of 2,000 sheets was used for each test. This supply was exhausted after 20 to 40 minutes for the mid-range dry-process machines evaluated. Collection of integrated chamber air samples continued for an additional four air changes (i.e., 2 hours for this study).
   - Power requirements. The type of outlet required varies among copiers. Therefore, installation of new outlets, changing outlets, or multiple outlet formats may be required.
   - Remote starting. Remote starting of the machines is necessary to maintain the integrity of the chamber. Complications from remote starting can result from either the software (automatic reset)

Table 6. Precision for emission rate measurements for copier 1 generated during triplicate tests.

Chemical	Idle		Print	
	µg/h • copier	% RSD	µg/h • copier	% RSD
VOCs				
Toluene	<10	-a	760	14
Butyl acetate	<10	-	50	13
Ethylbenzene	180	38	27,000	6.3
m,p-Xylene	160	38	29,000	5.7
Styrene	44	23	9,900	3.5
o-Xylene	88	28	17,000	3.9
Isopropyl benzene	<10	-	400	2.7
Propyl benzene	<10	-	790	0.7
a-Methyl styrene	13	9.4	1,100	6.9
n-Decane	12	15	450	13
2-Ethyl-1-hexanol	33	15	230	11
Limonene	<10	-	220	23
n-Nonanal	<10	-	1,100	13
n-Undecane	36	9.6	2,000	7.8
n-Dodecane	54	18	960	8
Aldehydes				
Butyraldehyde	<10	-	160	5.4
Benzaldehyde	<10	-	1800	11
Valeraldehyde	<10	-	540	10
n-Hexanal	<10	-	210	17
Ozone	ND b	ND	3000	7.1

a %RSD not calculated.
b Ozone concentrations were not observed in the idle mode.

Table 7. Estimated emission rates of selected VOCs, aldehydes, and ozone from dry-process photocopiers.

| | Emission Rate (µg/h · copier) | | | | | | | |
| | Idle | | | | Operation | | | |
Chemical	Copier 1	Copier 2	Copier 3	Copier 4	Copier 1	Copier 2	Copier 3	Copier 4
VOCs[a]								
Toluene	<10	74	<10	390	760	110	290	220
Ethylbenzene	180	<10	<10	10	28,000	360	2,400	<50
m,p-Xylene	160	23	48	<10	29,000	510	6,100	100
Styrene	40	47	220	49	9,900	3,000	12,000	300
o-Xylene	90	14	<10	<10	17,000	850	4,500	<50
Propylbenzene	13	<10	10	17	790	460	2,100	<50
a-Methylstyrene	12	<10	<10	24	330	<50	60	<50
n-Decane	33	<10	150	82	450	320	<50	62
2-Ethyl-1-hexanol	<10	93	130	11	230	5,600	14,000	130
Limonene	<10	<10	40	120	220	200	1,100	<50
n-Nonanal	36	<10	<10	49	1,100	3,900	3,600	2,000
n-Undecane	54	<10	<10	35	2,000	62	70	103
n-Dodecane	<10	<10	70	<10	960	82	120	75
Aldehydes/Ketones[b]								
Formaldehyde	<100	<100	<100	1,100	<500	<500	2,600	2,200
Acetaldehyde	140	<100	<100	<100	710	<500	960	1,200
Acetone	<100	<100	220	2,200	2,000	<100	<500	2,800
Propionaldehyde	<100	<100	<100	<100	<100	150	160	260
2-Butanone	<100	<100	<100	<100	<100	210	380	190
Butyraldehyde	<100	<100	<100	<100	160	<100	840	<100
Benzaldehyde	<100	<100	<100	<100	1,800	3,800	2,600	<100
Valeraldehyde	<100	<100	<100	<100	540	270	<100	250
n-Hexanal	<100	<100	<100	<100	210	100	1,200	440
Ozone	ND[c]	ND	ND	ND	3,000	1,300	4,700	7,900

[a] Measured by VOC Method.
[b] Measured by Aldehyde/Ketone Method.
[c] Ozone concentrations were not observed in idle mode.

and/or hardware (lack of electronic overdrive capability). These problems can be minimized if an experienced service technician installs, sets up, and checks out the equipment.

3. Dry-process photocopy machines can produce emissions of ozone and VOCs that can potentially have a significant impact on indoor air quality in an office or home environment. For the four machines tested, the compounds with the highest emission rates overall were ethylbenzene (28,000 µg/hour), m,p-xylenes (29,000 µg/hour), o-xylene (17,000 µg/hour), 2-ethyl-1-hexanol (14,000 µg/hour), and styrene (12,000 µg/hour). As an example, chamber air concentrations of styrene were about 100 µg/m³ for one machine. Since emissions testing was conducted using chamber conditions that might approximate conditions found in office buildings, it is likely the indoor air concentrations of this magnitude

would also be found in offices. For comparison, median indoor air concentrations for styrene measured about 1.0 µg/m³ in the Total Exposure Assessment Methodology (TEAM) study.[7]

4. Although many of the same compounds tended to be detected in emissions from each of the four photocopiers, the relative contribution of individual compounds varied considerably between machines, with differences greater than an order of magnitude for some compounds. The variation in compounds is most likely due to different toner formulations used for dry-process photocopy machines.

5. Some of the compounds detected in this study—benzaldehyde, ethylbenzene, nonanal, ozone, styrene, and xylenes—were consistent with compounds identified in the literature from photoimaging equipment. Again, the variation in compounds is most likely due to the

different toner formulations used for dry-process photocopy machines.

6. The ultimate goals from this research are a standardized guidance document on measuring indoor air emissions from office equipment and specific recommendations for reducing indoor air emissions from dry-process photocopy machines through pollution prevention strategies. Subsequent phases of this project that will be implemented to help accomplish these goals include:

- A round-robin study in three additional laboratories to help to evaluate the repeatability and comparability of the method in different chambers.
- Headspace and thermagravmetric analyses of different toners to determine the effects of toner type and age on emissions.
- The effect of copier print time on emission rates (i.e., time course data).
- Further analysis of the particulate data collected.
- Analysis of copier operating conditions that may affect emission rates.

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REFERENCES

1. Hetes, R.; Moore, M.; Northeim, C. Office Equipment: Design, Indoor Air Emissions, and Pollution Prevention Opportunities, EPA-600/R-95-045 (NTIS PB95-191375), U.S. EPA, Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, March 1995.
2. Brooks, B.O.; Davis, W.F., *Understanding Indoor Air Quality*, CRC Press, Boca Raton, FL, 1991.
3. Wollkoff, P. et al., "A study of human reactions to office machines in a climatic chamber," *Journal of Exposure Analysis and Environmental Epidemiology* 1992, 1(Suppl): 71-96.
4. National Institute of Occupational Safety and Health. *Indoor Air Quality and Work Environment Study, Library of Congress, Madison Building, Health Hazard Evaluation Report*, HETA 88-364-2104, Washington, D.C., 1991.
5. American Society for Testing and Materials (ASTM), ASTM D5116-90. *Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products*. Philadelphia, PA, 1990.
6. Buyers Laboratories, Inc. Copier Specification Guide, Hackensack, NJ, 1994.
7. U.S. EPA, Office of Acid Deposition, Environmental Monitoring, and Quality Assurance. Total Exposure Assessment Methodology (TEAM) Study, (NTIS PB88-100052), June 1987.

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Volatilization of Chemicals from Drinking Water to Indoor Air: Role of the Kitchen Sink

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ABSTRACT

Contaminated tap water is one source of potentially hazardous air pollutants in residential indoor air. Contaminants have been observed to volatilize from household tap water sources, including showers, wash basins, bathtubs, washing machines, dishwashers, and toilets. A background search of these sources led to the conclusion that more attention should be given to wash basins and tubs, the numerous operating conditions of which yield a significant range of chemical stripping efficiencies. In response, nine laboratory experiments were completed to determine chemical stripping efficiencies and mass transfer coefficients for a kitchen wash basin. Chemical stripping efficiencies ranged from 1.1% to 4.9% for acetone, 13% to 26% for toluene, and 18% to 48% for cyclohexane. The product of overall mass transfer coefficient and interfacial area (K_LA) ranged from 0.06 L/min to 0.24 L/min for acetone, 0.7 L/min to 1.9 L/min for toluene, and 0.9 L/min to 3.5 L/min for cyclohexane. Results clearly indicate that chemical properties (e.g., Henry's law coefficient) and system operating conditions (e.g., liquid flow rate and nozzle type) have a significant effect on contaminant stripping efficiency. Furthermore, significant gas-phase resistance can occur, even for relatively volatile contaminants, during some operating conditions. The latter observation has important implications with respect

to conventional protocols used to extrapolate radon data to other volatile contaminants in drinking water.

INTRODUCTION

In the United States, the average person spends 90% of his or her time indoors.[1] This statistic is significant, considering that concentrations of several contaminants observed in indoor air are often higher than in outdoor air. For example, median indoor-to-outdoor concentration ratios for 11 chemicals were reported to range from 0.5 to as high as 100 for two test sites, with an average of 12 for all chemicals.[2] The volatilization of chemicals from contaminated tap water may be a significant source of many indoor air contaminants. Maximum contaminant levels (MCL) for several volatile chemicals have been established by the U.S. Environmental Protection Agency (EPA). For example, the MCL for benzene in drinking water is 1 µg/L. Concentrations may significantly exceed this value in extreme cases (e.g., single-dwelling water wells contaminated by gasoline). Until recently, the focus of human exposure to toxic contaminants in tap water has been the ingestion pathway. However, a typical family of four in the United States uses 750 liters of water per day, of which only 0.4-2 liters is actually consumed per person.[3] Andelman[4] has estimated that the daily indoor inhalation exposure associated with contaminants originating in tap water may be as much as six times higher than ingestion exposure.

The current knowledge base with respect to volatilization rates associated with most indoor sources is limited. Past research has focused primarily on showers and washing machines.[5-11] Furthermore, the methodology employed in previous studies was often vague and lacked determination of associated mass transfer coefficients. The absence of reported experimental conditions is particularly significant with respect to understanding volatilization from wash basins and tubs, as these sources have a wide range of operating conditions that lead to several important gas-liquid mass transfer mechanisms. An understanding of the contribution of each of these mechanisms is important for the development of improved emissions models. The results of nine laboratory experiments completed to determine chemical stripping efficiencies and mass transfer coefficients for kitchen wash basins are presented in this paper.

IMPLICATIONS

Recent research related to volatilization of chemicals from drinking water to indoor air has focused on human inhalation in showers. Attempts to model chemical stripping have generally been based on simple extrapolation from well-studied compounds (e.g., radon to other chemicals) without a mechanistic understanding of fundamental mass transfer characteristics. The research described herein focuses on chemical emissions that occur during the use of kitchen wash basins. The influences of faucet and water flow characteristics, chemical properties, and the importance of gas-phase resistance to mass transfer were studied. Results should prove valuable for those involved with indoor exposure assessments and control analyses, and may also affect future decisions related to federal drinking water standards.