Evaluation of a Test Method for Measuring Indoor Air Emissions from Dry-Process Photocopiers

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ABSTRACT

A large chamber test method for measuring indoor air emissions from office equipment was developed, evaluated, and revised based on the initial testing of four dry-process photocopiers. Because all chambers may not necessarily produce similar results (e.g., due to differences in sink effects, temperature and humidity control, air exchange, pollutant monitoring, and measurement biases), a preliminary four-laboratory evaluation of the revised test method was conducted. To minimize variability, the evaluation used a single dry-process photocopier that was shipped to each of the four laboratories along with supplies (i.e., toner and paper).

The results of this preliminary four-laboratory evaluation demonstrate that the test method was used successfully in the different chambers to measure emissions from dry-process photocopiers. Differences in chamber design and construction appeared to have had minimal effect on the results for the volatile organic compounds (VOCs).

IMPLICATIONS

The paper discusses a four-laboratory evaluation of a large chamber test method developed by the authors to measure indoor air emission from dry-process photocopies. The results of the evaluation demonstrate that the test method was used successfully in the four different chambers to measure emissions from a dry-process photocopier, and that differences in chamber design and construction had minimal effects on the results for the volatile organic compounds (VOCs). The method can be used by manufacturers and others in order to evaluate emissions from copiers.

Perhaps more important than the chamber itself is the sample analysis as identified by duplicate samples that were analyzed by a different laboratory. Percent relative standard deviation (%RSD) was used to provide a simplistic view of interlaboratory precision for this evaluation. Excluding problems with suspected analytical bias observed from one of the laboratories, the precision was excellent for the VOCs with RSDs of less than 10% in most cases. Less precision was observed among the laboratories for aldehydes/ketones (RSD of 23.2% for formaldehyde). The precision for ozone emission rates among three of the laboratories was excellent (RSD of 7.9%), but emission rates measured at the fourth laboratory were much higher.

INTRODUCTION

Researchers, including Wolkoff et al.,[1] the National Institute for Occupational Safety and Health (NIOSH),[2] and Gallardo et al.,[3] have reported that the operation of office equipment can contribute to increased indoor air pollutant concentrations and has, in some cases, been associated with health complaints from exposed workers. As discussed by the authors in an earlier paper[4] and in a U.S. Environmental Protection Agency (EPA) report,[5] data in the literature are often collected using a variety of different methods, making it difficult to compare results from different laboratories.

To address the lack of a standard test method for measuring indoor air emissions from office equipment, the EPA's National Risk Management Research Laboratory and Research Triangle Institute (RTI) collaborated with several office equipment manufacturers to develop a large

chamber test method. The test method was based on the experience of the authors in product testing, on a published American Society of Testing and Materials (ASTM) test method,[6] and on existing test methods used by the participating manufacturers of office equipment. The EPA's objective in developing the test method was to ultimately encourage emission testing of office equipment by manufacturers and others with the hope that an increased understanding of emissions might encourage the development and manufacture of lower-emitting equipment (where applicable).

To evaluate and refine the method, testing was performed in two phases. Phase I was a single-laboratory evaluation of the test method at RTI using four different dry-process photocopiers.[4] Phase II was a four-laboratory evaluation of the method using one dry-process photocopier and is the topic of this paper. The purpose of Phase II was to provide a preliminary evaluation of the reproducibility of the test method in different chambers since the measurement of emissions from office equipment can be influenced by factors related to the chamber (e.g., sink effects, temperature and humidity control, air exchange, and pollutant monitoring methods) and to sampling and analysis.[7] The evaluation of the copier was intended to be representative of a "worst-case" scenario. That is, integrated chamber air samples were collected during copying of approximately 2,000 copies with sample collection continuing for a post-copying time period equal to four air changes. In this evaluation, intermittent operation of the copier was not studied.

Because large chamber testing is very complex, the primary objective of Phase II was to serve as a preliminary evaluation of the ability of the test method to meet predetermined data quality indicator goals for volatile organic compounds (VOCs), aldehydes/ketones, and ozone using different chambers and analytical methods. Data quality indicator (DQI) goals set for the interlaboratory comparison were selected to be typical for indoor air comparison studies. The DQI goals for precision are based on the percent relative standard deviation (%RSD) where RSD is equal to the standard deviation divided by the mean. The DQI goals for this evaluation are: VOCs $\leq$ 35%, aldehydes/ketones $\leq$ 35%, and ozone $\leq$ 25%.

The DQI goals for accuracy are based on percent recovery and are $\geq$ 70% for VOCs, aldehydes/ketones, and ozone. Evaluation of within-laboratory uncertainties was not a component of this preliminary evaluation. Rather, %RSD is used to provide a simplistic view of the interlaboratory precision. A larger study, that is, using at least six laboratories with multiple tests at each laboratory, would be needed to provide a definitive statement on the precision of the test method.[7]

METHODOLOGY

The four laboratories that participated in the evaluation have large chambers meeting the minimum size requirements for the test method (i.e., chamber dimensions of 1.4 times the dimensions of the copier) and appropriate analytical equipment.[4] Chamber characteristics are summarized in Table 1. To maintain control over copier-related variables, the same dry-process photocopier, whose emissions were measured in Phase I, was sent to the other three laboratories for testing and then returned to RTI as the final participant in the evaluation. Upon arrival at each laboratory, a manufacturer's service representative inspected, set up, and tested the copier to ensure that it was performing properly.

For the Phase II evaluation, one test was performed at each of the laboratories, with the exception of Laboratory 4. Three copier tests were performed at Laboratory 4 because of its own interest in evaluating the performance of its chamber for replicate tests. So as to not bias the evaluation data with the Laboratory 4 data, only results from the first test run at Laboratory 4 are presented here.

The sections below include an overview of the test method, the modification to the method for the Phase II testing, collection of chamber air samples, calculation of emission rates, the procedure followed for the chamber recovery experiments, and the method for headspace analysis of the toner.

Overview of Evaluation Test Procedure
The test method for the evaluation, as described in Reference 4 and summarized below, was provided to the participating laboratories along with quality assurance/quality control (QA/QC) instructions. A representative from

Table 1. Description of test chambers used in evaluation testing.

Laboratory	Volume (m³)	Construction Materials	Air System	Air-Exchange Rate (hr⁻¹)
Laboratory 1	22.7	Aluminum walls, stainless steel floor, Viton door seals	single pass	1.88
Laboratory 2	25.7	Aluminum walls, stainless steel & galvanized steel floor	single pass	1.75
Laboratory 3	35.4	Marlite walls & ceiling, vinyl floors	recirculating	0.904
Laboratory 4	29.1	Stainless steel	single pass	1.62

RTI went to each test facility at the time of testing to release standard emission sources into the test chamber. The standards release consisted of dosing the chamber with known levels of toluene, *n*-decane, formaldehyde, and ozone. The RTI representative also provided guidance with remote starting of the copier and toner depletion/replenishment (described below). However, personnel at each chamber facility were responsible for the chamber operation and sample collection and analysis, and the RTI representative did not provide assistance with chamber operation. Sampling cartridges were provided for the duplicates that were analyzed at RTI.

For the testing, toner from the same lot and copier paper from the same lot (recycled content of 25%) were used by all four laboratories. The same standard test pattern (representing 15% coverage of the paper) was used for all tests. Chamber temperature was maintained at 26-31 °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. Relative humidity (RH) within the chamber was maintained between 30 and 35%. A RH of 35% at 31 °C represents a mass of water equivalent to 50% RH at 23 °C.

The same sequence of operations was performed for each test:

Step 1. Service representative checked copier and assisted in setup of remote start.

Step 2. Toner depletion/replenishment was performed (see Test Method Modification for Phase II, below).

Step 3. Background air samples were collected from empty chamber.

Step 4. Copier was placed in chamber.

Step 5. Copier was powered up, paper was loaded in copier, and remote start was tested.

Step 6. Copier was equilibrated in chamber overnight in idle mode, that is, powered but not copying.

Step 7. Following the overnight equilibration, integrated chamber air samples were collected for the copier in the idle mode.

Step 8. Integrated chamber air samples were collected during full copier operation of 1998 copies (~38-min-operation time) and continued for a post-copying time period equal to four air changes (e.g., total sample collection time for a chamber operating at two ACH was 158 min).

Step 9. Air exchange rate was determined by injection of a tracer gas (e.g., carbon monoxide) during the test or other method.

Test Method Modification for Phase II

Phase I testing identified the need for one modification to the test method for the Phase II evaluation. During Phase I, data variability was observed for a single copier tested several times under the same chamber conditions. This occurred both during a changeover to toner from a new lot and when extended periods of time (one to three months) had elapsed between tests using the same toner cartridge. Toner from different lots was evaluated both by additional chamber testing and by headspace analysis[8] in order to identify the source(s) of the variation. Headspace concentrations from different toner lots were found to vary significantly; however, headspace concentrations were consistent within a given lot of toner. Additional chamber tests with operating photocopiers identified that the data variability was likely caused by residual toner that was retained in the toner delivery system of the copier between tests. Discussions with the manufacturer of this copier resulted in the recommendation that the old toner be depleted from the copier and then replenished with fresh toner when changing to a new toner cartridge or when approximately one month or more elapsed between tests using the same toner cartridge. Without the toner depletion/replenishment under these circumstances, toner from a new cartridge would be diluted by the toner still retained in the delivery system or the "old" toner would off-gas between tests, affecting emission results.

A procedure for toner depletion/replenishment was developed specifically for the photocopier used in the Phase II evaluation testing. To deplete the toner, the toner cartridge was removed from the copier and 3,500 copies of the standard image were made. As the toner in the delivery system was depleted, the image became very faint on the paper. To replenish the toner in the delivery system, a new toner cartridge was inserted into the copier and 500 copies of the standard image were made. At this point, the copy images appeared uniformly dark. To verify that the toner had been properly restored, a copy of the manufacturer's test pattern/image was made and compared against the original. This procedure appeared to be effective in "flushing" the older toner from the machine, replacing it with toner from the "fresh" cartridge. It is presumed that machine-specific depletion/replenishment procedures would need to be established experimentally for individual copier models. Some photocopiers or other types of office equipment may not allow depletion/replenishment of toners as easily as the copier that was used in this study.

Collection of Chamber Air Samples and Calculation of Emission Rates

All four chambers allowed for continuous operation of the copier and continuous sampling of chamber air without

opening the chamber during the test. Sampling points for the chamber air were selected to be representative of the chamber concentrations. When possible, a duplicate set of VOC and aldehyde samples were collected for analysis at RTI.

Methods used for collection and analysis of VOCs included various multisorbent tubes and Tenax cartridges. Each participating laboratory could use either method as long as adequate performance could be demonstrated. For each method, the sample volumes collected for analysis and sampling time were determined by the flow rate and analytical sensitivity required.

Although other methods could have been used, all laboratories used the silica gel/2,4-dinitrophenylhydrazine (DNPH) method for monitoring formaldehyde and other low molecular weight aldehydes/ketones.[9] Using this method, aldehydes/ketones were collected by passing chamber air through cartridges containing silica gel impregnated with DNPH. Formaldehyde and other aldehydes and ketones react with the DNPH to form the DNPH derivative and are collected on the cartridge material. With the DNPH method, care had to be taken to address the potential interference of ozone. Potassium-iodide-coated denuders or commercially available potassium iodide scrubbers were placed upstream of the DNPH cartridge to remove ozone.

For VOCs and aldehydes/ketones, chamber air samples were collected and analyzed for the target chemicals. For all tests, a chamber air sample was collected prior to placing the copier in the chamber (Step 3). A second chamber air sample was collected after the copier was placed in the chamber, powered up (but not printing), and equilibrated overnight in the chamber (Step 7). This second sample provided data on the equilibrium chamber air concentration in the idle mode. Finally, a third chamber air sample was collected from the time the copier started printing until four chamber air changes (approximately 2 hr) after printing was completed. This sample provided data on the average time-integrated chamber air concentration over the test period (Step 8).

Each laboratory stored collected samples in a manner consistent with its usual handling practices. At RTI, this consisted of storing the VOC cartridges in sealed glass tubes inside friction-sealed steel cans maintained at -10 °C. The DNPH cartridges were stored in sealed polypropylene jars supplied by the manufacturer and were maintained at 4 °C. These storage methods were recommended to the other participating laboratories.

Emission rates (ERs) for the idle and print modes, respectively, were calculated using chamber air concentrations as

$$ER_i = [(C_i - C_b) * V_c * A_c] / n \qquad (1)$$

where ER_i = emission rate in the idle mode in µg/hr × copier; C_i = measured chamber air concentration in the idle mode in µg/m³; C_b = measured background chamber air concentration in µg/m³; V_c = chamber volume in m³; A_c = chamber air-exchange rate in hr⁻¹; and n = number of copiers in chamber.

$$ER_c = [(C_p - C_i) * V_c * A_c * T_c] / (T_p * n) \qquad (2)$$

where ER_c = emission rate during printing in µg/hr × copier; C_p = measured time-integrated chamber air concentration during printing and post-copying period in µg/m³; T_c = time during which the sample was collected in hr; and T_p = time during which the copier was printing in hr.

Eqs 1 and 2 are based on the assumptions that the chamber is well mixed and there is no adsorption onto the chamber walls. Under these conditions, 99% of the chemicals emitted will have been purged from the chamber after 4 ACH. The first assumption was verified using the air-exchange data (Table 1), and the second assumption was evaluated using the recovery studies.

Chamber Recovery Experiments

Chamber dosing and recoveries were determined by introducing known amounts (E_{as}) of toluene, *n*-decane, formaldehyde, and ozone into the chambers at known rates. Chamber air samples were collected and analyzed using procedures identical to those used during the photocopier emission tests; however, the copier was not in the chamber during the recovery tests.[4] The measured amount of pollutant emitted during each test in mg, E_m, was calculated using:

$$E_m = (C_c * V_c * A_c * T_c) / T_s \qquad (3)$$

where C_c = measured chamber air concentration in µg/m³, and T_s = time during which the emission source was operating in hr⁻¹.

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

$$\%R = E_m / E_{as} * 100 \qquad (4)$$

where E_m = the amount measured during the recovery test in µg, and E_{as} = the amount that was introduced into the chamber during the test in µg.

Headspace Analysis of Toner

Toner samples of 50 mg were collected from each toner cartridge by the testing laboratory immediately following each copier emission test and sent to RTI for headspace analysis. These samples were collected so that the chemical consistency of the different toner cartridges from the

same lot could be compared. A sampling kit with detailed instructions was provided, and the collected samples were held at room temperature in tightly sealed vials until analysis. Headspace analysis procedures were the same as those used during Phase I testing[7] except that the temperature during Phase II testing was 150 °C.

RESULTS

The results of the emission rate measurements for VOCs, aldehydes/ketones, and ozone in the printing mode are discussed in the following sections. Results from the four photocopiers tested in Phase I indicate that emission rates are consistently much lower (e.g., often orders of magnitude and, in the case of ozone, not detected) in the idle mode than in the print mode.[4] Consequently, results are presented here only for the print mode.

Results of the duplicate analysis, chamber recovery experiments, and headspace concentrations of the toner are also discussed.

VOC Emission Rate Measurements

The results of the VOC emission rate measurements generated by each laboratory during copier operation are shown in Table 2 and Figure 1. For all of the tests, the compounds with the highest emission rates were ethyl benzene, *m,p*-xylene, *o*-xylene, and styrene. Results show very good general agreement among laboratories for most compounds. The precision among Laboratories 1, 2, and 4 was excellent with RSDs of 3.5% for ethyl benzene, 4.4% for *m,p*-xylene, 14.6% for *o*-xylene, 7.9% for total xylenes, and 3.4% for styrene. (RSDs were calculated only for the chemicals where

emissions from all laboratories are greater than 1,000 µg/hr. Emissions less than 1,000 µg/hr are too close to the detection limit for a good comparison of results between the laboratories.) These RSDs meet the DQI goal that was set for this evaluation (VOCs ≤ 35% RSD). These RSDs are also well within the range of RSDs for the analysis of VOCs and aldehydes/ketones. They are also much better than RSDs obtained in a previous small chamber interlaboratory comparison study that evaluated VOC emissions from polyvinyl chloride (PVC) flooring materials and from a water-based floor wax.[10] Twenty laboratories participated in that study, and RSDs for the PVC flooring materials ranged from 26 to 42%. The scatter was higher for the water-based floor wax.

Table 2. Emission rates measured during copier operation—selected VOCs (µg/hr copier).

| Chemical | Phase II | | | | Phase I |
	Lab 1	Lab 2	Lab 3	Lab 4	RTI
Toluene	440	1100	-[a]	370	760
Ethyl benzene	23000	24000	32000	22000	28000
Styrene	6100	6600	9600	6200	9900
m,p-Xylene	21000	23000	-[b]	21000	29000
o-Xylene	11000	14000	-[b]	10000	17000
Total Xylenes	32000	37000	46000	31000	46000
Isopropyl benzene	140	220	-	-	-
n-Propyl benzene	340	480	-	390	790
a-Methyl styrene	500	790	-	660	330

[a]Represents data not listed for one of the following reasons: not reported by laboratory; below calibration range; or not detected.

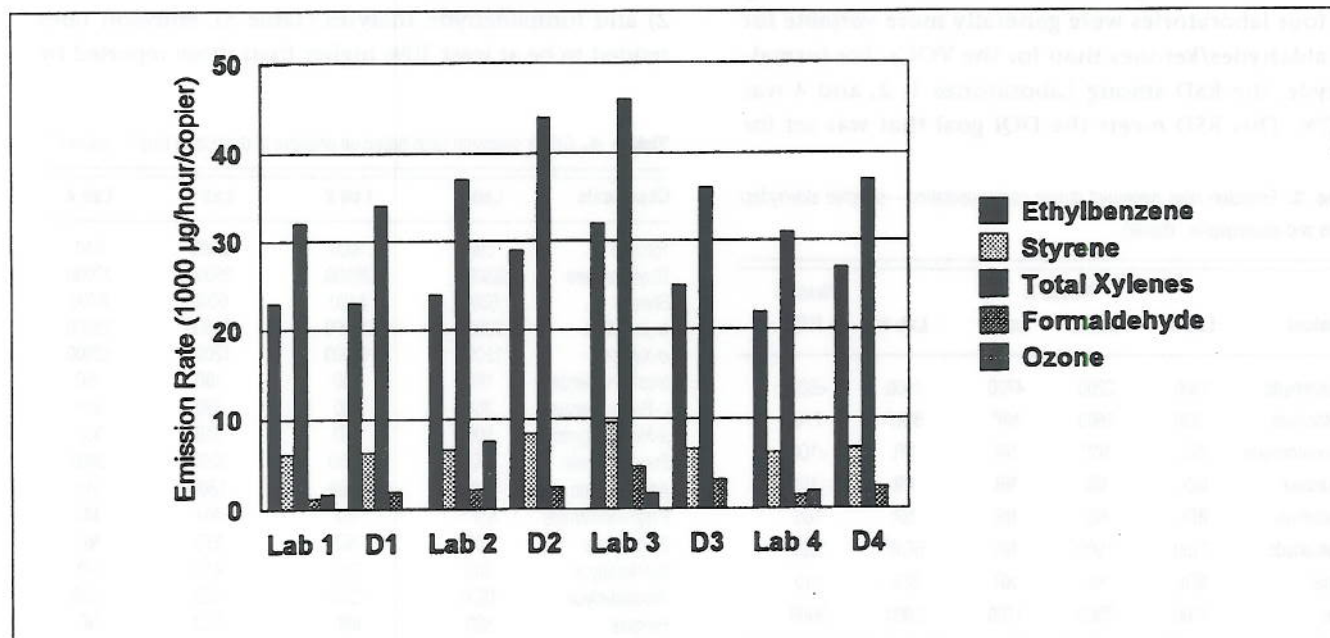[b]Laboratory 3 reported total xylenes only, not individual isomers.

Figure 1. Emission rates measured during copier operation (µg/hr/copier). D1-D4 refer to duplicate samples from Laboratories 1–4, respectively, analyzed by RTI. Duplicates are not corrected for idle concentrations because duplicates were not collected during idle mode.

As discussed below, the results of the duplicate analysis suggest that the higher emission rates observed for Laboratory 3 are due to a laboratory measurement bias. If the results from Laboratory 3 are included in the calculation of precision, the RSDs increase to 15.7% for ethyl benzene, 16.3% for total xylenes, and 20.2% for styrene. However, if the RSDs are calculated instead, using the duplicate samples for Laboratory 3 that were analyzed at RTI (rather than the samples analyzed by Laboratory 3), the RSDs are considerably better: 4.3% for ethyl benzene, 6.7% for total xylenes, and 3.2% for styrene.

The results for the Phase I testing at RTI are also shown in Table 2 for a general comparison between Phases I and II. The results obtained from Phase II are generally comparable with the Phase I results from RTI; however, note that the toner depletion/replenishment procedure was amended to the test method for the Phase II testing so a rigorous comparison between the two phases is not appropriate.

Aldehydes/Ketones Emission Rate Measurements

The results of the aldehydes/ketones emission rate measurements generated by each evaluation laboratory during copier operation are shown in Table 3 and Figure 1. For all of the laboratories, emission rates were the highest for formaldehyde and benzaldehyde. However, all four evaluation laboratories were not able to provide complete results for all of the aldehydes/ketones for various reasons, as noted in Table 3 (i.e., below detection limit, not detected, below calibration range).

For the data reported, the measurements among the four laboratories were generally more variable for the aldehydes/ketones than for the VOCs. For formaldehyde, the RSD among Laboratories 1, 2, and 4 was 23.2%. This RSD meets the DQI goal that was set for

this evaluation (aldehydes/ketones ≤ 35% RSD). However, when the data for Laboratory 3 are included, the RSD more than doubles to 55.9%. The RSD is 36.3% if the duplicate sample is used (to account for the suspected analytical bias for Laboratory 3). RSDs were not calculated for any other aldehydes/ketones because of the limited data. The poorer precision observed for the aldehydes/ketones are probably due to the relatively low aldehydes/ketones emissions measured (i.e., close to method detection limits).

Ozone Emission Rate Measurements

The results of the ozone emission rate measurements during copier operation are shown in the bottom row of Table 3 and in Figure 1. The measured ozone emission rates for Laboratories 1, 3, and 4 were consistent at 1,700, 1,700, and 2,000 µg/hr · copier, respectively. The RSD for these measurements is 7.9%. This RSD meets the DQI goal that was set for this evaluation (ozone ≤ 25% RSD). However, including the ozone emission rate measured by Laboratory 2, which was much higher (7,500 µg/hr · copier), increases the RSD tenfold to 76.6%.

Analysis of Duplicates

Results of the duplicate samples collected in the individual laboratories and analyzed by RTI are shown in Table 4 and Figure 1. As noted in Table 4 and Figure 1, idle concentration data were not collected for the duplicate samples analyzed by RTI. As a result, the duplicate measurements tend to be slightly higher than the emission rates calculated using eq 2.

When Laboratory 3 conducted its own VOC (Table 2) and formaldehyde analyses (Table 3), emission rates tended to be at least 30% higher than those reported by

Table 3. Emission rates measured during copier operation—selected aldehydes/ketones and ozone(µg/hr · copier).

| Chemical | Phase II | | | | Phase I |
	Lab 1	Lab 2	Lab 3	Lab 4	RTI
Formaldehyde	1300	2200	4700	1500	<500
Acetaldehyde	390	1600	NR[a]	BDL[b]	710
Propionaldehyde	BDL	ND[c]	NR	NR	<100
2-Butanone	BDL	ND	NR	NR	<100
Butraldehyde	BDL	ND	NR	NR	160
Benzaldehyde	1100	1800	NR	BCR[d]	1800
Hexanal	BDL	ND	NR	BDL	210
Ozone	1700	7500	1700	2000	3000

[a]NR = not reported; [b]BDL = below detection limit; [c] ND = not detected; [d]BRC = below calibration range.

Table 4. Copier emission rates based on analysis of duplicates (µg/h · copier).[a]

Chemicals	Lab 1	Lab 2	Lab 3	Lab 4
Toluene	590	1000	2000	540
Ethyl benzene	23000	29000	25000	27000
Styrene	6300	8400	6600	6700
m,p-Xylene	22000	29000	24000	25000
o-Xylene	12000	15000	12000	12000
Isopropyl benzene	160	160	160	150
n-Propyl benzene	360	460	390	370
a-Methyl styrene	500	730	550	550
Formaldehyde	1900	2400	3200	2400
Acetaldehyde	1100	1300	1300	510
Propionaldehyde	ND[b]	ND	ND	ND
2-Butanone	600	ND	570	ND
Butraldehyde	300	280	410	ND
Benzaldehyde	1500	1200	980	1000
Hexanal	590	690	950	ND

[a]Values not corrected for idle concentration; idle samples not collected for analysis by RTI; [b]ND = not detected.

the other laboratories. However, the duplicate emission rate data for Laboratory 3 (Table 4) were in general agreement with results from the other laboratories (with the exception of toluene, which was higher). The results of this duplicate analysis suggest that higher emission rates observed for samples analyzed by Laboratory 3 are due to measurement bias in the analysis at Laboratory 3 rather than chamber performance.

Chamber Recovery Experiments
The calculated percent recoveries for the recovery tests are presented in Figure 2 for VOCs, aldehydes, and ozone. The figure includes recovery data for samples analyzed at the individual laboratories and for samples analyzed at RTI. The percent recoveries are the result of the release of the standard emission sources, which were conducted using the same chamber conditions as when the copier was tested. General recoveries for toluene and *n*-decane are very good for Laboratories 1, 2, and 4 (note that *n*-decane was not released at Laboratory 2). The high percent recoveries for the samples analyzed at Laboratory 3 are probably due to the analytical bias observed at this laboratory.

Recoveries of formaldehyde at Laboratories 1 and 4 are very good (greater than 90%) as is the recovery at Laboratory 3 for the sample analyzed at RTI (84%). The reason for the low recovery of formaldehyde at Laboratory 2 is unknown. However, it may be due to the complicated system required for formaldehyde delivery at this location, or there could have been an unobserved (due to the fact that one cannot see into this chamber) malfunction of the system. The emission rates for formaldehyde measured during the test at Laboratory 2 (Table 3), as well as the duplicate samples from the test analyzed by RTI (Table 4), show formaldehyde levels consistent with those measured at the other laboratories. This gives further support that the low recoveries from Laboratory 2 are likely related to the recovery test itself and not a problem with the Laboratory 2 chamber or analysis.

Ozone recoveries were 25, 55, 62, and 86%. The low recoveries for ozone are probably due to the ozone's reacting with the surface of the chamber. The DQI goals for accuracy are based on percent recovery and were set at ≥ 70% for VOCs, aldehydes/ketones, and ozone. These goals were generally met for the VOCs at all of the laboratories and for formaldehyde at Laboratories 1, 3, and 4. However, the goals were not met for formaldehyde at Laboratory 2 or for ozone at Laboratories 1, 2, and 3.

Toner Headspace Concentrations
Results of the headspace samples are shown in Table 5. These results are reported in nanograms per milliliter of headspace and show no major differences in the concentrations from the toner cartridges used at Laboratories 1,

3, and 4. The toner sample from Laboratory 2 was held for approximately three months prior to being analyzed. Volatile losses may have occurred during this time as indicated by the lower headspace results for this sample.

SUMMARY AND RECOMMENDATIONS
The results from this evaluation are very good considering that the tests were conducted over a four-month period, the copier was shipped thousands of miles, tests were conducted in a variety of chambers, and different analytical methods were used. The results of this four-laboratory evaluation demonstrate that the test method can be used successfully in different chambers to measure emissions from dry-process photocopiers. The results and recommendations for future research include:

(1) The test method used in Phase I was amended for Phase II with a procedure for toner depletion/replenishment. Without the depletion/replenishment of the toner, the toner from a new cartridge could be diluted by the toner still retained in the delivery system. The procedure developed appeared to be effective in "flushing" the older toner from the machine, replacing it with toner from the "fresh" cartridge. It is presumed that machine-specific depletion/replenishment procedures would need to be established experimentally for individual copier models.

(2) The VOC results from the four different, large chamber laboratories are comparable. The VOCs reported to have the highest emission rates by all of the participating laboratories were ethyl benzene, followed by *m,p*-xylene, *o*-xylene, and styrene. Excluding problems with the suspected analytical bias seen from Laboratory 3, the precision between laboratories for the VOCs was excellent with RSDs of less than 10% in most cases.

(3) All four evaluation laboratories were not able to provide complete results for all of the aldehydes/ketones for various reasons (i.e., below detection limit, not detected, below calibration range). However, for all of the laboratories, emission rates were the highest for formaldehyde and benzaldehyde. For formaldehyde, the precision between Laboratories 1, 2, and 4 was higher than for the VOCs with an RSD of 23.2%.

(4) The measured ozone emission rates for Laboratories 1, 3, and 4 were consistent at 1700, 1,700, and 2,000 µg/hr · copier, respectively. The RSD for these measurements is 7.9%. However, the emission rate measured by Laboratory

Table 5. Toner headspace concentrations from toner cartridges used in evaluation study (ng/mL headspace).

Chemical	Lab 1	Lab 2[a]	Lab 3	Lab 4
Toluene	4.0	0.8	2.1	3.3
Ethyl benzene	620	260	460	580
Styrene	200	100	140	180
m,p-Xylene	620	270	440	570
o-Xylene	410	210	300	380
Isopropyl benzene	6.6	3.8	5.0	6.2
n-Propyl benzene	14	9	21	14
a-Methyl styrene	28	23	22	33

[a]Sample held for –3 months; volatile losses may have occurred during this time.
Note: All headspace analyses were performed at RTI.

2 was much higher at 7,500 μg/hr · copier.

(5) Differences in chamber design and construction at the four laboratories seemed to have minimal effect on the test results for VOCs and formaldehyde. Perhaps more important than the chamber construction is the analytical methodology used to analyze the samples as identified by the duplicate samples.

(6) Percent recovery for VOCs at Laboratories 1, 2, and 4 were very good. High percent recoveries for Laboratory 3 are probably indicative of the analytical bias observed at this laboratory. Recoveries of formaldehyde at Laboratories 1, 3, and 4 were very good. However, the recovery of formaldehyde at Laboratory 2 was very low—

probably due to a problem with the recovery test at this laboratory. Ozone recoveries were 25, 55, 62, and 86%. The low recoveries for ozone are probably due to the ozone's reacting with the surface of the chamber.

(7) While the test method developed and evaluated focused on VOCs, aldehydes/ketones, and ozone emissions, further attention should be given to the measurement of particle emissions from copiers. Limited particle data collected for two copiers in previous tests 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.[4] Also, other researchers have measured elevated particle emissions from copiers.[11,12] Particle measurements were not a focus of this study because of the complexity of generating known masses of particles (which would be required for the method evaluation).

(8) A larger study, that is, using at least six laboratories with multiple tests at each laboratory, should be conducted to provide a definitive statement on the precision of the test method.[7] The results from this evaluation will be useful in designing such a study and addressing critical variables among the laboratories (e.g., analytical methods, ozone recovery).
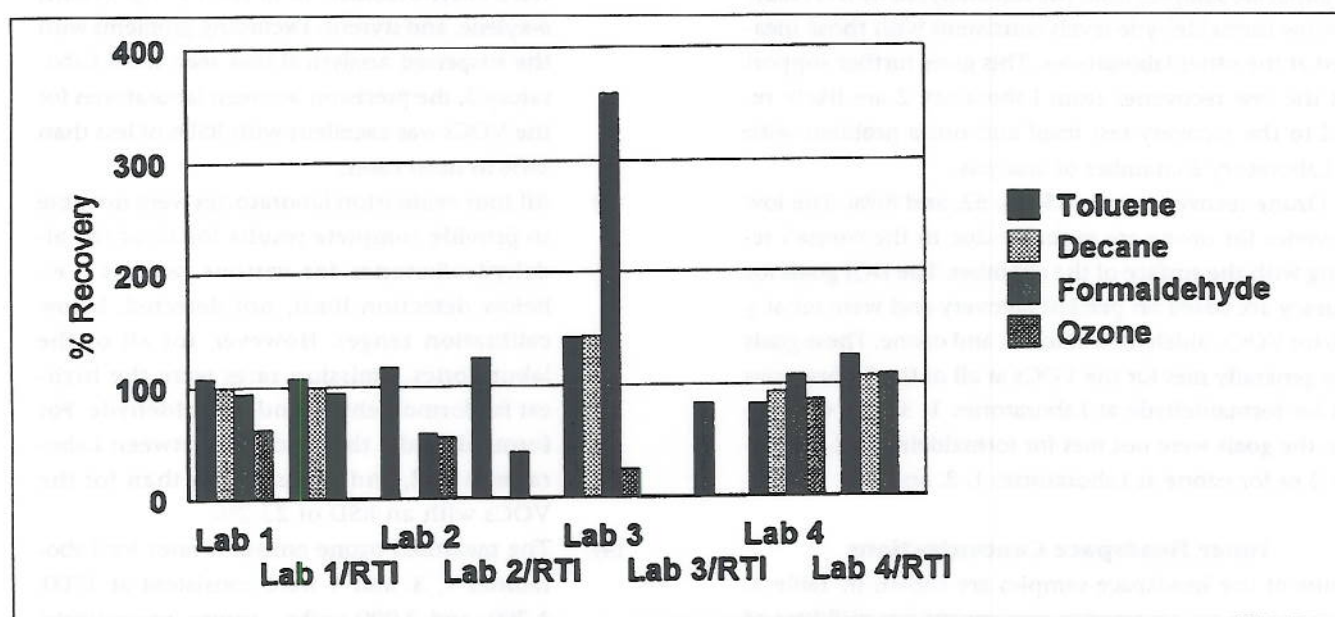
Figure 2. Chamber recoveries based on standard emission sources (μg/hr). Data labeled "/RTI" indicate samples analyzed at RTI; ozone recoveries were not measured by RTI; decane was not included in standard released at Laboratory 2; and toluene and decane data for "Lab 3/RTI" were not reported due to low internal standard area counts in sample.

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