Chemical Emissions: A Quantitative Approach to Product Stewardship for Printers in the 21st Century

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Abstract

IBM's product stewardship program for printer chemical emissions is described. This program ensures chemical emissions from printing products comply with standards such as California Proposition 65, OSHA Permissible Exposure Limits, and others. This is accomplished by performing environmental chamber tests that measure chemical emissions emanating from printers. An overview of IBM's chamber testing program is discussed, along with methods developed to interpret chemical emissions data obtained from environmental chamber testing of printers. International chamber testing consensus methods are identified.

Introduction

Printer environmental attributes are increasingly important measures of value and customer acceptance. Ecolabels exist for certifying low chemical-emitting printers and supplies (#2669 BAM, 2006; Nordic Swan, http://www.svanen.nu/Eng/criteria/kriterie.asp?pgn=015; Green Seal http://www.greenseal.org/certification/environmental.cfm; Japan Life Cycle Assessment http://web-japan.org/trends96/honbun/tj960806.html; EU Eco-label http://www.eco-label.com/default.htm). Ecolabels may restrict chemicals that are used during manufacturing, chemicals that are contained in the finished product, and chemicals that are emitted from the product or supplies. Existing regulations are cause for assurance that chemicals which may emanate from products are acceptable to the work environment. These include, in the United States, the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs) and The State of California Safe Drinking Water and Toxic Enforcement Act of 1986, also known as California Prop 65, No Significant Risk Levels (NSRLs) and Maximum Allowable Dose Levels (MADLs). The American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs®) are widely recognized as recommended occupational standards, and serve as occupational health guidelines.

Chemical emissions emanating from printers have been studied and reported (Kagi, 2007; Lee, 2001 and 2006; Zhou, 2003; Tuomi, 2000; Brown, 1999; Leovic, 1996; Wolkoff, 1993). Consensus methods for measuring chemical emissions emanating from printers have recently been developed (BAM, 2006; ECMA, 2006; JIS, 2006). Reproducible measurements of printer chemical emissions among different laboratories have been demonstrated (Leovic, 1998). This paper discusses chamber test method parameters, room modeling, and occupational health criteria evaluation to meet product regulation requirements.

Materials

Estimating potential chemical emissions in a customer environment is most accurately achieved by testing a new, production-level product. Packaging materials may influence compounds identified during the chamber test, and these materials should be removed prior to testing. Hardware components of newly manufactured products contain finite amounts of residual compounds. ECMA 328 provides for operating products up to 24 hours prior to testing to allow for the decay of a portion of these residual compounds. While not applicable to printers, JEITA (Japan Electronics and Information Technologies Industries Association) chamber testing method allows for operating hardware for up to 5 hours prior to conducting a chamber chemical emissions test (JEITA, 2006).

Chamber size and ventilation rate influence the concentrations of emitted compounds in the chamber. It is desired to achieve sufficient chamber concentrations of emitted compounds to permit measurement with the selected sampling and analytical technique. Three chamber sizes are available to accommodate a wide range of IT products tested: 667 L, 101 m^3, and 254 m^3. ECMA 328, Blue Angel, and JIS X 6936 provide for product to chamber volume ratios (commonly referred to as "loading factor") of 1:4 to 1:100. This is to be regarded as a guideline, relying on the scientists' analysis of product heat load, chamber volume, chamber ventilation rate, sampling flow rate, analytical limits of quantitation, (LOQ) modeled room parameters, and applicable chemical standards to determine the appropriate combination of these test parameters.

Chambers are constructed of Summa® polished stainless steel, stainless steel, and enameled aluminum. Instruments used to monitor chamber environmental conditions and to conduct air sampling are calibrated with traceability to the U.S. National Institute of Standards and Technology (NIST).

Methods

Chamber Testing

IBM currently follows modified test methods described in ECMA 328, 2nd Edition, 2006. This method has been harmonized with the BAM 2005 Blue Angel method, and is similar to JIS X 6936, 2005 for major test parameters.

Chambers are cleaned using deionized water or an alkaline detergent prior to each product test. Following cleaning, chambers are allowed to passivate for three days. This passive ventilation period has been associated with reduced residual chamber concentrations of aldehydes. Background chemical concentration levels are determined the day prior to the chamber test in an empty chamber following purging with filtered air for at least 4 air changes. The background concentration of each compound identified as an emissions chemical is subtracted from the chamber concentrations identified during the test. The three previously cited standards, ECMA 328, BAM Blue Angel, and JIS X 6936, prescribe an air sampling regimen intended to result in obtaining the average chamber concentration of emissions chemicals. IBM currently ascribes to a modified chamber air sampling regimen collecting chamber air samples at equal interval. Interval samples are collected with sample midpoint times of 15, 45, and 75 minutes for printers that can contain enough paper to print for 75 minutes. Printers that are not capable of printing for 75 minutes are operated for the maximum printing time achievable at the highest speed attainable, and interval samples collected accordingly.

Samples for VOCs (volatile organic compounds, generally regarded as non-polar compounds with boiling points ranging from 80 – 200° C.), are collected following EPA Methods TO-1 and TO-17 (EPA, 2007). 500 mg Tenax® TA sorbent is loaded into ¼ inch I.D. stainless steel tubes. Triplicate samples of volumes approximating 1, 2, and 4 L are collected at each time interval. Analyses are conducted using GC/MS (gas chromatography – mass spectroscopy). Media blank and field blank samples are collected, and a Student's t-test performed on the results to gain a confidence at the 99% upper bound limit. These blank values are subtracted from each sample tube. All peaks over the limit of quantitation (LOQ) are identified. A concentration-toxicity screening algorithm (EPA, 1989) was developed to identify the compounds most likely to contribute significantly to risks. Always included are all compounds provided with a PEL, NSRL, or MADL. Five-point calibration curves using "neat" or "authentic" standards are generated for each compound included in the algorithm. When "neat" standards are not available, a structural surrogate is used. At an LOQ equaling an area count of 300,000, a chamber concentration of approximately 2 $\mu g/m^3$ is attainable for most compounds.

Formaldehyde and acetaldehyde are measured following EPA Method TO-11A. SKC #226-120 sorbent tubes are used. The sorbent is DNPH coated silica gel. Analysis is conducted using high pressure liquid chromatography. An LOQ of 40 ng/tube is attainable using this method. A sample time of 30 minutes at a flow rate of 0.775 Lpm will yield a sample LOQ of 1.7 $\mu g/m^3$.

Ozone is monitored using a Dasibi model 1008 direct reading instrument. This monitor operates on the principle of absorption of ultraviolet light by ozone. The instrument LOQ is 2 ppbv.

Particulates are monitored using two methods. For screening evaluations, a Miniram Model PDM-3 forward light scattering direct reading instrument is placed near the paper exit of the printer, which is anticipated to be the highest source of particulate emissions. Alternatively, gravimetric air sampling using a 0.8 µm pore size PVC filter is used. Gast electric vacuum pumps operating at 10 – 15 Lpm are placed on each side of the printer. Gravimetric analysis of 20 - 50 µg per filter yields LOQs of 22 – 83 $\mu g/m^3$ with a sample time of 60 minutes.

Room Modeling

It is desired to obtain average chamber concentrations of identified emissions chemicals from which room concentration simulations can be performed. Methods of determining average chamber concentrations can be complex, and are based on the number and duration of chamber air samples collected during the chamber test. Methods are contained in the three standards previously cited: ECMA 328, BAM Blue Angel, and JIS X 6936. IBM follows the method of Tichenor (Tichenor, 2001) to calculate emission rates using a mass balance approach. The mass balance equations are:

$$\frac{dC}{dt} = LR_{(t)} - NC \tag{1}$$

$$R_{(t)} = \frac{NC + dC/dt}{L} \tag{2}$$

Where:

$R_{(t)}$	=	emission rate at time t; (ug/hr/product)
N	=	chamber air exchange rate; (hr^{-1})
C	=	chamber concentration at time t; (ug/m^3)
dC/dt	=	change in chamber concentration with respect to time
L	=	one unit per m^3 calculated as 1/V; V is the effective chamber volume

Thus emission rates are calculated for each interval sample allowing the average and maximum emission rates to be determined. The average emission rate is determined using an equal interval weighting approach following:

$$R_{(t)}\,avg = \frac{R_{(0.25)} + R_{(0.75)} + R_{(1.25)}}{1.5} \tag{3}$$

Average emission rates are then used to model estimated room concentrations which are utilized as the potential exposure doses for comparison with occupational standards. The modeled room concentrations assume one standard volume per printer based on average office size or recommended installation area, and ventilation rate. The ventilation is further assumed to be well-mixed. ASHRAE Standard 62.1-2004 (ASHRAE, 2004) provides for a design occupant density of 5 persons per 1000 ft^2. Assuming a 9 ft. ceiling height, the minimum occupant design density is 51 m^3 per person. The design outdoor air flow per person stipulated in ASHRAE 62.1-2004 of 17 cfm per person equates to 0.57 ACH in a 51 m^3 office. The median building ventilation rate in U.S.

office buildings as determined by Persily is approximately 1.0 ACH (air change per hour) (Persily, 1989). The predicted room concentrations do not account for interzonal flow in multi-compartment buildings nor adsorption and re-emission from construction materials, furnishings, and equipment. Room concentrations are determined assuming equilibrium is reached in the room using the method of Mølhave (Mølhave, 1982):

$$RC = \frac{R_{(avg)}\ n}{V\ N} \quad (4)$$

Where:

- RC = room concentration of emissions chemical ($\mu g/m^3$)
- $R_{(avg)}$ = average emission rate of emissions chemical ($\mu g/hour$)
- n = number of products in room (unitless)
- V = room volume (m^3)
- N = room ventilation rate ($hour^{-1}$)

Standards Evaluation

Emission rates of identified emissions compounds derived during chamber testing may be used to compare printers, or different supplies within the same printer. Room concentrations calculated using measured emission rates of identified emissions compounds can be utilized as potential exposure doses to compare with occupational health standards such as PELs and TLV®s. NSRLs and MADLs are provided in terms of mass per day. Evaluating calculated room concentrations to them requires converting room concentrations to an exposure dose. This is accomplished by making reasonable assumptions about inhalation rates and exposure durations. Average room concentrations can be modified proportionately based on the daily printing duty cycle when a printer is not intended to print continuously during the work day, and thus modify the room concentration prior to comparison with occupational standards.

Discussion

Testing a new, production-level product will ensure that residual compounds existing in hardware components are measured. However, emission rates of these compounds will decrease with power-on time (U.S. EPA, 1995; Davis, 2007). Emissions from printer supplies (toner, paper) are constant, and are related to printing speed, fusing temperature, room temperature, and print density. These are not affected by the age of the printer, assuming that the printer is functioning within specified parameters. With limitations noted, calculation of room concentrations of individual compounds yields a quantitative tool that can be used to assess printer chemical emissions attributes against standards or voluntary guidelines. Mathematical modeling per Equation 4 can accommodate multiple units in a room of given volume and ventilation rate. This is useful for determining compliance with the above standards, and can be adapted to evaluating unique situations such as multiple devices in a classroom.

Disclaimer

Methods and procedures presented in this paper are not intended as, nor should not be construed as, legal or regulatory advice. Mention of specific materials or equipment in not intended to endorse their use. Prior results from these procedures do not guarantee a similar outcome in other locations or with other devices.

References

ASHRAE Standard 62.1-2004: "Ventilation for Acceptable Indoor Air Quality". American Society of Heating, Refrigerating, and Air-Conditioning Engineers, 2004. 99

BAM (Blue Angel) : "Test Method For the Determination of Emissions from Hardcopy Devices with respect to awarding the environmental label for office devices according to RAL-UZ 122; 2006 (http://www.blauer-engel.de/englisch)

Brown, S.: "Assessment of Pollutant Emissions from Dry-Process Photocopiers". Indoor Air, vol. 9, pp. 259-267, 1999.

Davis, W.: "Time-Related Decay in VOC Emissions from a high performance IT Product: Impact of Decay on the Quantitative Assessment of potential Risks associated with Product Emissions". American Industrial Hygiene Association Conference and Exposition, Philadelphia, Pennsylvania, USA, June, 2007.

European Computer Manufacturers Association (ECMA) International: Standard ECMA-328 2nd ed., "Determination of Chemical Emission Rates from Electronic Equipment". www.ecma-international.org; June, 2006.

Henschel, D., Fortmann, R.: "Potential for Reducing Styrene Exposure from Copied Paper through Use of Low-Emitting Toners". Journal of the Air and Waste Management Association, vol. 53, pp. 1347-1354, November, 2003.

Henschel, D., Fortmann, R.: "Variations in the Emissions of Volatile Organic Compounds from the Toner for a Specific Photocopier". Journal of the Air and Waste Management Association, vol. 51, pp. 708-717, May, 2001.

JEITA Japan Electronics and Information Technologies Industries Association: "VOC Guidelines for Personal Computers (Ver. 1)". PC-VOC-G-2005; January, 2006.

Japanese Industrial Standard (JIS): JIS X 6936: 2005. "Information technology – Office equipment – Measurement of ozone, volatile organic compounds and dust emissions rate from copiers, printers and multi-function devices"; 2005.

Kagi, N., Fujii, S., et. al.: "Indoor Air Quality for Chemical and Ultrafine Particle Contaminants from Printers". Building and Environment, vol. 42, issue 5, pp. 1949-1954, 2007.

Lee, C., Dai, Y., et. al.: "Characteristics and Health Impacts of Volatile Organic Compounds in Photocopy Centers". Environmental Research, vol. 100, issue 2, pp. 139-149, 2006.

Lee, C., Lam, S., Fai, H.: "Characterization of VOCs, Ozone, and PM_{10} Emissions from Office Equipment in an Environmental Chamber". Building and Environment, vol. 36, pp. 837-842, 2001.

Leovic, K., Sheldon, L., et. Al.: "Measurement of Indoor Air Emissions from Dry-Process Photocopy Machines". Journal of the Air and Waste Management Association, vol. 46, pp. 821-829, September, 1996.

Leovic, K., Whitaker, D., Northeim, C., Sheldon, L.: "Evaluation of a Test Method for Measuring Indoor Air Emissions from Dry-Process Photocopiers". Journal of the Air and Waste Management Association, vol. 48, pp. 915-923, October, 1998.

Mølhave, L.: "Indoor Air Pollution due to Organic Gases and Vapours of Solvents in Building Materials". Environment International, v8, pp. 117-127, 1982.

National Research Council (NRC): "Risk Assessment in the Federal Government. Managing the Process". National Academy Press, Washington, D.C. 1983.

Persily, A.: "Ventilation Rates in Office Buildings". Indoor Air Quality 1989, San Diego.

Tichenor, B.: "Review of 667 L Dynamic Chamber Test Facilities, Methods, and Procedures at IBM Center for Process and Product Toxicology – Boulder, CO". IBM Internal document, 2001.

Tuomi, T., Engström, B., et. Al.: "Emission of Ozone and Organic Volatiles from a selection of Laser Printers and Photocopiers". Applied Occupational and Environmental Hygiene, vol. 15, number 8, pp. 629-634, 2000.

U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Interim Final Risk Assessment Guidance for Superfund, Vol. 1: Human Health Evaluation Manual, OSWER Directive 9285.7-01a, September 29, 1989.

U.S. Environmental Protection Agency, Office of Research and Development, Office Equipment: Design, Indoor Air Emissions, and Pollution Prevention Opportunities, EPA-600/R-95-045, March, 1995.

U.S. Environmental Protection Agency, Technology Transfer Network, Ambient Monitoring Technology Information Center, http://www.epa.gov/ttn/amtic/airtox.html; 2007.

Wolkoff, P., Wilkins, C., et. al.: "Comparison of Volatile Organic Compounds from Processed Paper and Toners from Office Copiers and Printers: Methods, Emission Rates, and Modeled Concentrations". Indoor Air, vol. 3, pp. 113-123, 1993.

Zhou, J., Chen, W., Tong, G.: "Ozone Emitted during Copying Process – A Potential Cause of Pathological Oxidative Stress and Potential Oxidative Damage in the Bodies of Operators". Biomedical and Environmental Sciences, vol. 16, number 2, pp. 95-104, June, 2003.

Biography

William Davis has been a member of IBM's product chemical emissions testing team for 15 years. The team has tested over 400 products during this time. Mr. Davis is a Certified Industrial Hygienist by the American Board of Industrial Hygiene, and holds a Master of Science Degree in Environmental Engineering from Drexel University, USA.