| TEXTE | 75/2013

ENVIRONMENTAL RESEARCH OF THE
FEDERAL MINISTRY OF THE ENVIRONMENT,
NATURE CONSERVATION AND NUCLEAR SAFETY

Project No. (FKZ) 3708 95 301
Report No. (UBA-FB) 001743/E

Measurement of Fine and Ultrafine Particles from Office Devices during Printing in order to Develop a Test Method for the Blue Angel Ecolabel for Office-Based Printing Devices

Summary

by

Dr. Mathias Barthel
Dr. Stefan Seeger
Dipl.-Ing. Monika Rothhardt
Dr. Olaf Wilke
Dr. Wolfgang Horn
Elevtheria Juritsch
Dr. Oliver Hahn
Dr. Oliver Jann

Bundesanstalt für Materialforschung und –prüfung (BAM), Germany

On behalf of the Federal Environment Agency (Germany)

UMWELTBUNDESAMT

This publication is only available online. It can be downloaded from http://www.uba.de/uba-info-medien-e/4567.html along with the complete and a German-language version.

The contents of this publication do not necessarily reflect the official opinions.

ISSN 1862-4804

Study performed by:	Bundesanstalt für Materialforschung und –prüfung (BAM) Fabeckstr. 44-46 12203 Berlin, Germany
Study completed in:	August 2011
Publisher:	Federal Environment Agency (Umweltbundesamt) Wörlitzer Platz 1 06844 Dessau-Roßlau Germany Phone: +49-340-2103-0 Fax: +49-340-2103 2285 Email: info@umweltbundesamt.de Internet: http://www.umweltbundesamt.de http://fuer-mensch-und-umwelt.de/
Edited by:	Section III 1.3 Eco-design, Environmental Labelling, Environmentally Friendly Procurement Dr. Jörn-Uwe Thurner

Dessau-Roßlau, August 2013

Summary

The continuous public debate on possible adverse health effects of fine (FP) and ultrafine particle (UFP) emissions from laser printing devices (LPD) induced the German Federal Environment Agency (UBA) to initiate a research project aimed at developing a test method for particle counting under standard conditions in environmental test chambers. As an outcome, the particle counting was integrated into the draft of the test method for emission measurement (RAL-UZ-122, Annex S-M) of the German Blue Angel ecolabel to laser printing devices, as well as the test standards ECMA-328 and the draft of ISO/IEC 28360. The procedure was successfully tested in an international round robin.

On this basis, the award criteria and values for the emission of fine and ultrafine particles in the framework of the Blue Angel ecolabel can be agreed and product tests can be performed.

As a result of the secondary aim of the project, some particle sources within laser printing devices were identified by the coupling of analytical methods. The identified source contributions, the analysis of the chemical composition of the particles and their size distributions add to the knowledge on these emissions and may enhance the environmental risk assessment in comparison with other aerosol sources. This project was preceded by two research projects carried out by the BAM Division 4.2 whose results have been published under the numbers 71/03 and 35/08 of the UBA text series.

The currently (in 2011) valid award criteria RAL-UZ-122 deal with the material emissions TVOC, ozone, benzene, styrene and gravimetrically measurable dust under standard conditions in emission test chambers. To integrate the number-based measurement of particle emissions, the following aspects needed to be clarified in a research programme:

- Clarification of the influence of methodological factors on particle measurements using different aerosol devices and in emission test chambers of different sizes and types
- Comparison of printers with different emission behaviour
- Comparison of different methods of data analysis

A reference pool of selected printing devices was set up for the investigations, whose main technical parameters are listed in Table S1.

Table S1: Reference pool for office devices

LPD	Type	Manu-facturer	Volume (m³)	Printing speed (Pages/minute) colour	monochrome	Type of ventilation
1	Printer	A	0.09	20	20	N/A.
2	MFD	B	0.09	5	24	N/A.
3	Printer	C	0.04	-	25	Blower
4	Printer	A	0.05	-	32	Suction
5	Printer	D	0.04	-	18	Blower
6	Printer	E	0.05	7.5	7.5	N/A.
7	Printer	B	0.08	-	33	Blower
8	Printer	F	0.09	21	21	Blower
9	Printer	G	0.03	-	23	Blower
10	MFD	A	0.11	-	21	Blower

MFD: multifunction device; A, B, C, D, E, F, G: manufacturer code

The pool devices were procured from spring 2009. Seven manufacturers are represented in the pool. The pool represents various new fuser technologies and toner systems. Within the project, no individual analysis of the fuser technologies and toner systems in the pool devices was performed. The devices have small to medium volumes and performances and meet all the requirements of the applicable RAL-UZ-122 for tests in a 1-m³ chamber. The *blower* type ventilation indicates an active air-ejection by a fan from at least one housing opening. Accordingly, the *suction* type ventilation includes at least one housing opening where air is sucked actively by a fan. Devices marked with N/A do not allow the identification of the type of ventilation without opening the housing.

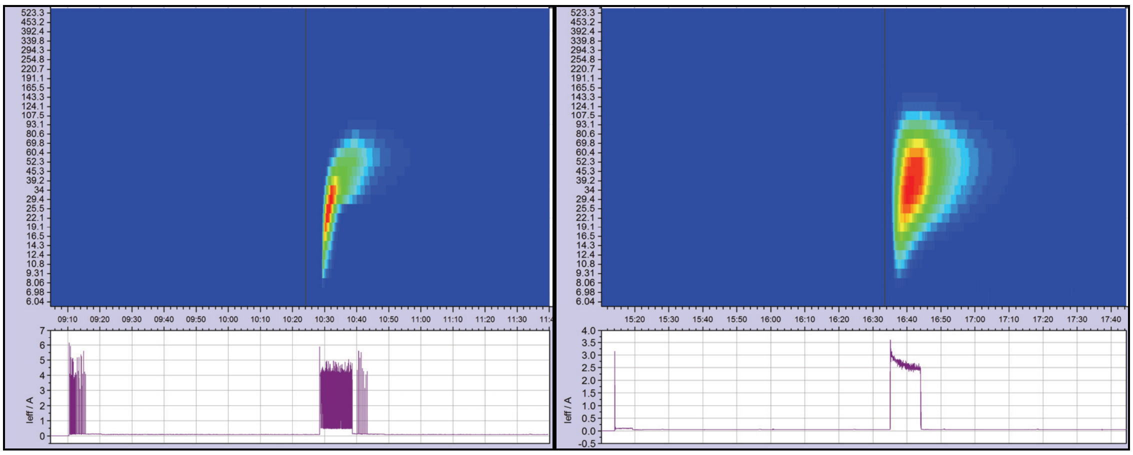
Model:

In the laser printing process, black and/or coloured toner powder with typical grain sizes above 1 µm is attracted by means of a static electrical charge from the toner cartridge to the paper. This creates the print image which is immediately fixed thermally to the paper in the so-called fuser unit at about 150-200 °C. This process includes the melting of the applied toner powder, a substantial thermal and mechanical effect on the paper and the heating of some components of the laser printer such as the fuser unit, transfer rollers, etc. During the printing process, volatile substances are vaporised and released as gases, some of these gases then create particles by cooling and recondensation. The particles are transported as aerosols by the air flow within the laser printing device out of the housing and then into the environment.

The aerosol emissions from LPD of the device pool were measured several times under comparable conditions in emission test chambers with 1 and 5 m³ volume using aerosol measurement devices. Both accumulated particle number concentrations and size distributions of the number concentration of particles up to 20 µm in diameter were recorded as functions of time. In all measurements, only one type of pre-conditioned office paper and OEM toner cartridges were used exclusively.

Physical Analysis of Particle Emissions:

Particulate emissions from LPD differ significantly in timing, number and size distribution. These differences are not due to methodological factors or boundary conditions of the measurements such as chamber size, air exchange rate, aerosol measurement instrument types, rather they reflect properties intrinsic to the type of LPD. Figure S1 shows an example of two different particle emission spectra, recorded during the stand-by and printing phase, respectively (see definitions below).



LPD7, Spectrum type 1 LPD10, Spectrum type 2

Vertical axes top: Particle diameter D_p [nm] in 32 logarithmically distributed particle size classes. Particle number concentration: linear colour codes, dark blue: lowest values, red: highest values. Horizontal axes: time [hh:mm]. Vertical axes bottom: current consumption [Ampere].

Figure S1: Particle size spectra of LPD7 and LPD10

Particles emitted from LPD have diameters less than 300 nm. Contributions above 300 nm particle diameter to the total number of emitted particles are without exception within the detection limit range of the aerosol counting measurement techniques applied and can be neglected in the case of a number-based approach. In the studied pool in particular, no contributions to the particle number concentration were generally detected in the size range above 1 µm. Thus toner powder with typical diameters > 1 µm in the aerosols emitted from LPD is not detectable as a particulate fraction. This finding confirms BAM's previous results which were obtained on a wider variety of office devices. The particulate emissions are very reproducible in terms of time graphs, size distributions and number concentrations when the conditioning steps and boundary conditions specified in detail in the test methods are adhered to. The standard deviation of the quantitative results is LPD-type dependent. A comparison of measurement devices showed a good agreement of butanol condensation particle counters (B-CPC) and so-called fast sizers (e.g. EEPS, FMPS). Water-based CPCs (W-CPC) show a partially reduced counting efficiency for aerosols from the LPD. They are therefore not proposed to be used in the test procedure.

Test Methods and Evaluation Criteria:

Due to the observed different particle size distributions and their rapid changes over time, an evaluation criterion which differentiates according to particle size classes does not make much sense. Therefore, the accumulated particle number concentration *Cp(t)* is considered as the primary measurand in a particle size range that includes at least the size interval 7-300 nm relevant to particle emissions from LPD. In the present project, a quantitative evaluation method based on the primary measurand *Cp(t)* was developed. This proposal was introduced by BAM to the Technical Committee TC38 "Product-related environmental attributes / TG1 Chemical Emissions" of the industrial association ECMA during the project period where it was debated and, after modifications, adopted in December 2010 as ECMA 328 Standard "Determination of Chemical Emission Rates from Electronic Equipment (5th edition)". The draft of the test method RAL-UZ-122, Appendix S-M submitted at the completion of the UFOPLAN project is harmonised in its substantial parts with ECMA 328, but contains useful specific options and simplifications for the tests in the context of the Blue Angel.

It was possible to integrate the particle emission measurement into RAL-UZ-122, Appendix S-M, as well as ECMA 328 to complement the test catalogue while maintaining the existing test procedure for chemical emissions. Therefore, no separate measurement of particle emission is required. The evaluation method for particle emissions according to RAL-UZ-122, Appendix S-M calculates the number of particles emitted in the printing phase *TP*, from the primary measurand as the primary benchmark for the quantification of particle emissions. Here, the volume of the test chamber and particle losses due to air exchange and other processes are considered. For comparison with a test value, *TP* can be related to the number of printed pages, thus the benchmark *TP/pp* [-] is defined (pp stands for printed page). The draft test method RAL-UZ-122, Annex S-M uses the standard printing time of 10 minutes as a reference thus the average rate of PER_{10} [particles per 10 minutes printing time] can be established as a benchmark. Other benchmarks can, in principle, be derived based on *TP*. Figure S2 shows the integration of particle emission measurement into the test procedure according to RAL-UZ-122, Appendix S-M.

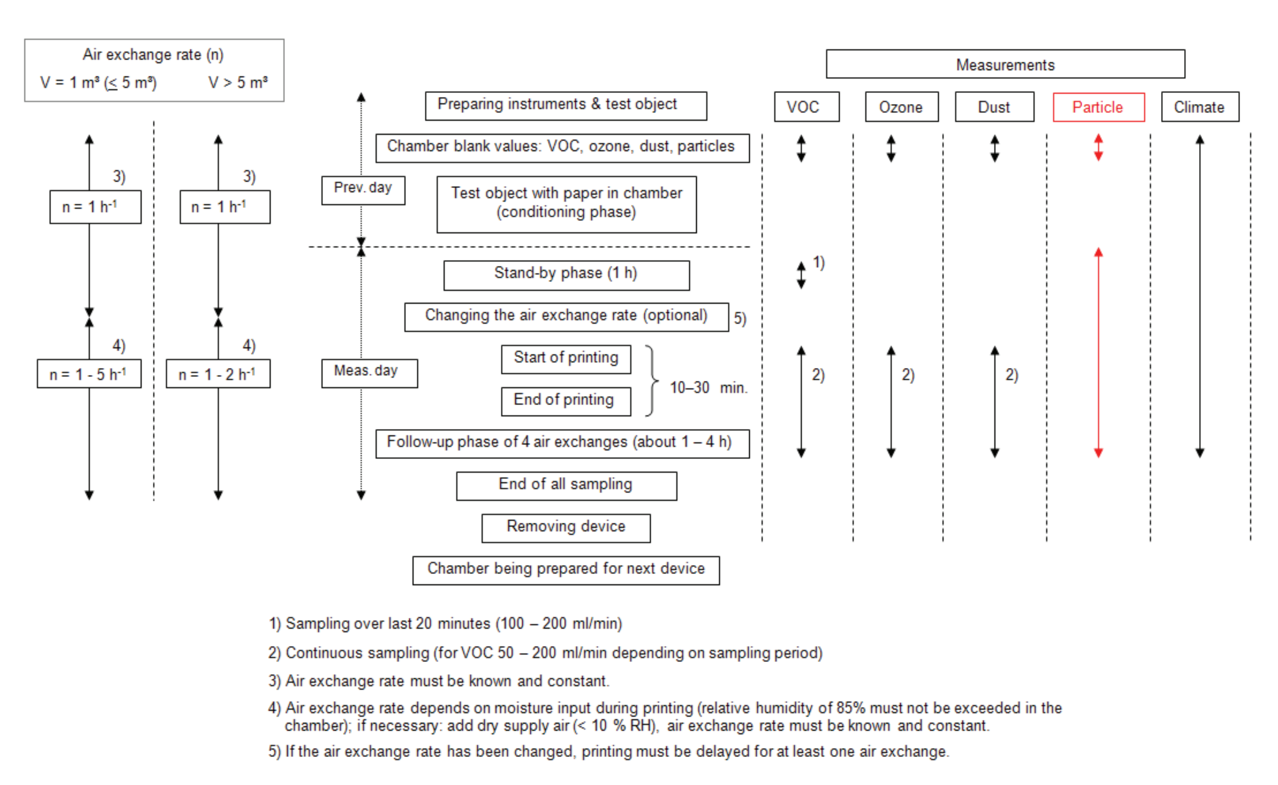


Figure S2: Integration of particle emission measurement (red) in the test procedure according to RAL-UZ-122, Appendix S-M

Table S2 shows the results of the particle emission measurements in the pool for the benchmark PER_{10}. The pool devices could be significantly differentiated based on the test and evaluation scheme in terms of their particle emission behaviour. Feasibility of the test and evaluation were confirmed by an interlaboratory comparison with six participants and two LPD from the project device pool. Another result of the collaborative study is the good comparability of the quantitative results.

Table S2: Results of particle emission measurements for the benchmark PER_{10} [particles/10 minutes]

LPD	**1**		**2**		**3**	**4**	**5**	**6**		**7**	**8**		**9**	**10**
Mode	mono-chrome	colour	mono-chrome	colour	mono-chrome	mono-chrome	mono-chrome	mono-chrome	colour	mono-chrome	mono-chrome	colour	mono-chrome	mono-chrome
PER_{10} (arithm. average)	2.2E11	7.6E11	2.8E11	8.7E11	**2.9E12**	1.2E12	6.4E11	**2.3E9**	3.0E9	1.0E12	9.1E11	1E12	5.2E11	1.2E11

bold: Maximum & minimum values

Result Summary - Chemical Analysis of Particulate Emissions:
The airborne particulate emissions from the LPD were separated by size using a 13-stage cascade impactor and made available to a size-dependent qualitative chemical analysis. The analysis was performed by combining the complementary procedures micro-X-ray fluorescence spectroscopy (µXRF, sensitive to elements) and thermodesorption gas chromatography-mass spectrometry (TD-GC-MS, sensitive to volatile organic substances).

The XRF analysis identified the elements silicon (Si), sulfur (S), chlorine (Cl), calcium (Ca), titanium (Ti), chromium (Cr), iron (Fe), bromine (Br) and traces of nickel (Ni) and zinc (Zn) as constituents of the aerosols from laser printing devices. The investigation of paper, toner, and structural components using XRF resulted in the attribution of certain elements to potential particle sources: thus, Ca-containing aerosol components can be attributed primarily to paper dust, while Si, Cr, Fe, Ni and Zn aerosol components are assigned to toners. It is suspected that there are Si aerosol constituents of siloxanes. Evidence of substantial concentrations of bromine (Br) in the structural components of the printers suggests a connection between brominated flame retardants and Br contents in two of the ten aerosols tested.

Within the GC-MS analyses, mainly alkanes, alkenes, siloxanes, phthalates and esters were identified as aerosol components. A brominated compound was detected in the aerosol of one of the printers.

Studies of the materials involved in the printing process enable the observed SVOCs to be attributed to certain sources: while long-chain alkanes (C_{20} – C_{36}) were primarily found in the toner, long-chain esters were identified in the paper. In addition, alkenes with chain lengths of C_{18} – C_{22} were detected which sometimes also occur in the aerosols.

Plastic parts are suspected to be the sources of phthalates, while siloxanes are attributed to their use as lubricants. However, it was not possible to unambiguously prove this attribution in any of the cases.

In the structural components, brominated compounds were found which are believed to be in connection with their use as brominated flame retardants and may be the cause of the compound detected in the aerosol. The available data do not allow for a conclusive assessment to be made.
Investigations into the volatility of the deposited particles have led to the identification of non-volatile residues after heating the aerosol to 400 °C. It can be concluded in combination with the

knowledge on the element composition of the particulate emissions that solid inorganic particles make up a portion of the total particle number in the order of magnitude of 1%.

Table S3: Size-resolved results of XRF analysis of aerosols of the devices tested

d_{50} (nm)	30	60	100	160	270
LPD 1			Ca*		
LPD 2		Ca*, Cr, Fe, Ni*			
LPD 3		Ca*			
LPD 4				Ca*	
LPD 5	Ca	Ca	Ca*		
LPD 6					
LPD 7		Si*, S*, Ca, Br*	Si, S, Cl, Ca Cr*, Fe*, Zn*, Br	Si, S, Cl* Ca, Zn*, Br	
LPD 8			Si	Si, Ca	Si, Cl*, Ca Ti*, Fe
LPD 9		Cl*, Fe, Br*	Si, Cl*, Ca Ti*, Fe, Br	Ca, Ti* Fe*, Br*	
LPD 10		Ca*	Ca	Ca*	

* Element detectable in traces only; empty cells: concentration below detection limit
Attribution to sources: paper (blue), toner (green), structural components (yellow)

Table S4: XRF results of four toner samples tested

Toner sample of LPD:	XRF results of toner samples
3	Si, Sn, Ca, Ti, V, Cr, Mn, Fe
5	Si, Sn, Ca, Ti, V, Cr, Mn, Fe, Ni, Zn
7	Ca, Ti, V, Cr, Mn, Fe, Zn
9	Si, Ca, Ti, Cr, Fe

Table S5: Results of GC-MS analysis of toner samples

Toner sample of LPD:	GC-MS results
1	Benzenedicarboxyl acid ester, aromatic compounds, 1-heptacosanol, alkanes (C21 – C35)
2	Styrene, propenoic acid ester, benzaldehyde, 1-dodecene, 1-chloro dodecane, benzophenone, alkanes (C16 – C32)
3	Phenol, acetophenone, biphenyl, alkanes (C15 – C34), benzoic acid ester, aromatic compounds
4	Aromatic compound, benzene propanoic acid ester, alkanes (C29 – C36)
5	1-Octanol, phenoxypropanol, aromatic compounds, alkanes (C20 – C32)
6	Styrene, aromatic compounds, alkanes (C24 – C35)
7	2-Allylphenol, benzenedicarboxyl acid ester, terephthalic acid ester, alkanes (C22 – C28)
8	1-Tridecene, cyclododecane, ether, C21 alkane, propenoic acid ester, squalane, C24 alkene
9	Cyclohexadecane, hexadecane acid, aromatic compound, propenoic acid ester, C27 alkane, squalene, cholesterol
10	Acetophenone, butenoic acid ester, aromatic compounds, alkanes (C29 – C35)