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

Research Report 201 95 311/02
UBA-FB 000510/E

Texte
88
03
ISSN
0722-186X

Development of a Test Method for and Investigation into Limiting the Emissions from Printers and Copiers within the Framework of Assigning the Environmental Label

by

Dr. Oliver Jann
Jens Rockstroh
Dr. Olaf Wilke
Reinhard Noske
Doris Brödner
Uwe Schneider
Dr. Wolfgang Horn
Federal Institute for Materials Research and Testing (BAM)
Laboratory IV.22, Emission from Materials

On behalf of the Federal Environmental Agency

UMWELTBUNDESAMT

Publications by the Federal Environmental Agency
in the TEXTE series are available subject to advance
payment of **10,00 Euro** by bank transfer, crossed cheque
or paying-in form to

Account number 432 765-104 at the
Postbank Berlin (Sorting Code 10010010)
Fa. Werbung und Vertrieb
Wolframstraße 95-96,
12105 Berlin

At the same time please direct your written order to the Firma Werbung und Vertrieb naming the ***volume number*** *from the TEXTE series, and the* ***name*** *and* ***address*** *of the orderer.*

Translated by Nigel Pye, NP Services, nrpye@blueyonder.co.uk
English translation edited by Tamas Meggyes, BAM, Tamas.Meggyes@bam.de

Publisher: Federal Environmental Agency (Umweltbundesamt)
Postfach 33 00 22
14191 Berlin
Tel.: +49/30/8903-0
Telex: 183 756
Telefax: +49/30/8903 2285
Internet: http://www.umweltbundesamt.de

Edited by: Section III 1.3
Brigitte Jacobs

Berlin, January 2004

Berichts-Kennblatt

1. Berichtsnummer UBA-FB	2.	3.

4. Titel des Berichts
Entwicklung einer Prüfmethode und Untersuchungen zur Begrenzung von Emissionen aus Druckern und Kopiergeräten im Rahmen der Umweltzeichenvergabe

5. Autor(en), Name(n), Vorname(n)
Dr. Oliver Jann, Jens Rockstroh, Dr. Olaf Wilke, Reinhard Noske, Doris Brödner, Uwe Schneider, Dr. Wolfgang Horn

6. Durchführende Institution (Name, Anschrift)

Bundesanstalt für Materialforschung und -prüfung (BAM),
Laboratorium IV.22 „Emission aus Materialien“, 12200 Berlin

7. Fördernde Institution (Name, Anschrift)

Umweltbundesamt, Postfach 33 00 22, D-14191 Berlin

8. Abschlußdatum
28.02.2003

9. Veröffentlichungsdatum

10. UFOPLAN-Nr.
201 95 311 / 02

11. Seitenzahl
159

12. Literaturangaben
68

13. Tabellen und Diagramme
33

14. Abbildungen
79

15. Zusätzliche Angaben
Dem Bericht liegt das im Rahmen des Forschungsvorhabens entwickelte Prüfverfahren für die Bestimmung von Emissionen aus Hardcopygeräten im Anhang bei.

16. Kurzfassung
An neun verschiedenen Hardcopygeräten wurden in unterschiedlichen Emissionsmesskammern (zwei verschiedene 1 m³ - Kammern und eine 20 m³ - Kammer) in Kombination mit geeigneten Probenahme- und Analysenverfahren Untersuchungen zum Emissionsverhalten dieser Geräte hinsichtlich Staub, Ozon und VOC (TVOC) durchgeführt. Luftprobenahme und Analytik erfolgten für VOC mittels Tenax TA und anschließender Thermodesorption (TDS) in Verbindung mit GC / MS. Ozon wurde kontinuierlich bestimmt. Der Ozonanalysator arbeitete auf der Grundlage der flammenlosen Reaktion von Ozon mit Ethylen nach dem Prinzip der Chemilumineszenz. Die Staubbestimmung erfolgte gravimetrisch mittels Glasfaserfilter und Ultramikrowaage. Zusätzlich wurde die Partikelemission während des Druckbetriebes mit einem Partikelzähler bestimmt. Aufgrund der technischen Rahmenbedingungen standen nur kurze Druckzeiten von maximal 36 Minuten zur Verfügung. Um die Gleichgewichtskonzentration in der Prüfkammer zu erreichen, wurde die Luftaustauschrate in den 1 m³ - Kammern auf n = 4,0 bis 4,7 pro Stunde erhöht.
Zusätzlich zur Prüfung in den Emissionsmesskammern sind verschiedene Papiere mittels Direkt - TDS sowie unterschiedliche Toner mittels Headspaceprobenahme in Kombination mit GC / MS hinsichtlich ihres Emissionsverhaltens untersucht worden.
Für die untersuchten Geräte wurden Emissionsraten ermittelt. Sie betrugen für TVOC 0,41 bis 22,4 mg pro Stück und Stunde, für Ozon kleiner 0,02 bis 4,6 mg pro Stück und Stunde sowie für Staub 0,10 bis 7,63 mg pro Stück und Stunde. Verglichen mit Frischfaserpapier wurden bei den Untersuchungen mit Recyclingpapier deutlich höhere SVOC - Konzentrationen nachgewiesen.
Im Ergebnis der Untersuchungen wurde ein Prüfverfahren entwickelt, das die Basis für Emissionsmessungen im Rahmen der Umweltzeichen RAL –UZ 62, RAL –UZ 85 sowie des neuen RAL –UZ 114 für Multifunktionsgeräte darstellt.

17. Schlagwörter
Emissionen, VOC, Ozon, Staub, Hardcopygeräte, Drucker, Kopierer, Emissionsmesskammer, Umweltzeichen

18. Preis	19.	20.

Report Cover Sheet

1. Report No.
UBA-FB

2.

3.

4. Report Title
Development of a test method and investigations for determining emissions from printers and copiers in the framework of the German Environmental Label

5. Autor(s), Family Name(s), First Name(s)
Dr. Oliver Jann, Jens Rockstroh, Dr. Olaf Wilke, Reinhard Noske, Doris Brödner, Uwe Schneider, Dr. Wolfgang Horn

6. Performing Organisation (Name, Address)

Federal Institute for Materials Research and Testing
Laboratory IV.22 „Emission from Materials“, 12200 Berlin

7. Sponsoring Agency (Name, Address)

Umweltbundesamt, Postfach 33 00 22, D-14191 Berlin

8. Report Date
28.02.2003

9. Publication Date

10. UFOPLAN-Ref. No.
201 95 311 / 02

11. No. of Pages
159

12. No. of Reference
68

13. No. of Tables, Diagrams
33

14. No. of Figures
79

15. Supplementary Notes
The testing method for the determination of emissions from hardcopy devices developed within the framework of the research project is enclosed in the report's appendix.

16. Abstract

The emission behaviour with regard to dust, ozone and VOC (TVOC) of nine different hardcopy devices in combination with suitable air sampling and analysis procedures was investigated in different emission test chambers (two different 1 m³ - chambers and one 20 m³ - chamber). Air sampling and analysis for VOC were done by means of Tenax TA and subsequent thermal desorption (TDS) in connection with GC / MS. Ozone was determined continuously. The ozone analyser worked on the basis of the flame rid reaction of ozone with ethylene according to the principle of chemiluminescence. The dust determination was done gravimetrically by means of glass fibre filter and an ultra micro - balance. Additional the particle emission during the printing process was measured with a particle counter. The general technical conditions of the tested hardcopy devices were the reason for short printing times with a maximum of 36 minutes. In order to achieve the equilibrium concentration in the test chambers the air exchange rate in the 1 m³ - test chambers had to be increased to a value of n = 4,0 to 4,7 per hour.
Additional to the examination of the hardcopy devices in the emission test chambers different papers were investigated by means of direct - TDS and different toners were tested by means of head space sampling in combination with GC / MS.
For the examined hardcopy devices emission rates were determined. The emission rates for TVOC ranged from 0,41 to 22,4 mg per piece and hour, for ozone from less than 0,02 to 4,6 mg per piece and hour and for dust from 0,10 to 7,63 mg per piece and hour. The comparison between recycling paper and paper produced from primary fibres showed in general higher SVOC emissions from recycling paper.
As the result of the investigations a test method for the determination of emissions from hardcopy devices was developed. This test method is the basis for emission tests in the framework of the German Award of the Environmental Label for office devices RAL -UZ 62, RAL -UZ 85 and the new RAL -UZ 114 for multifunctional devices.

17. Keywords

Emissions, VOC, Ozone, Dust, Hardcopy devices, Printers, Copiers, Emission test chamber, Environmental Label

18. Price

19.

20.

Environmental Research Programme
of the Federal Ministry for the Environment,
Nature Conservation and Nuclear Safety

Project No (UFOPLAN) 201 95 311 / 02

Development of a Test Method for and Investigation into Limiting the Emissions from Printers and Copiers within the Framework of Assigning the Environmental Label

by

Dr. Oliver Jann, Jens Rockstroh,
Dr. Olaf Wilke, Reinhard Noske, Doris Brödner, Uwe Schneider, Dr. Wolfgang Horn

Federal Institute for Materials Research and Testing (BAM)
Laboratory IV.22, Emission from Materials

COMMISSIONED
BY THE FEDERAL ENVIRONMENTAL AGENCY (UBA)

June 2003

Contents

1 Preamble

The research project underlying this report was supported by means of the Environmental Research Programme of the Federal Environmental Agency as a subproject within the ‘Feasibility Studies for New Environmental Labels (RAL - UZ) per ISO 14024 [12] for Selected Groups of Products’ topic.

Issues concerning the emission behaviour of hardcopy devices, conclusions for a test method and the preliminary results of the project were presented and discussed in three meetings of a project-advisory working group. The members of the working group, which convened in a small or large group depending on the topic, belonged predominantly to research and/or testing institutes, equipment manufacturers and the Federal Environmental Agency (UBA). The names of all members of this expert panel are listed in Section 15.7 in the Appendix.

The members of the expert panel have provided helpful guidance to the project, which is gratefully acknowledged. Contribution by companies that made investigation material available within the framework of the project is also acknowledged.

2 Introduction

2.1 Background and objectives

Since human beings live a predominant part of their life indoors, such as living and bedrooms, offices, schools and kindergartens, special importance is given to the quality of the air that they must breathe.

In order to improve the indoor air quality it is necessary to gain information about the contribution to the overall emission of individual emission sources and purposefully reduce emissions. Furnishing materials, building products, furniture, printers and copiers belong to the main emission sources in the interior. An identification of the emission behaviour of the products used in interiors can only be performed under standardised test conditions in emission test chambers or cells.

The ENV-13419 Part 1 and 2 standard [21], [22] was developed for VOC emission test chambers and cells based on the European - Collaborative - Action (ECA) - Reports Nr. 8 [17]. An efficient sampling and analysis method based on Tenax sampling, consecutive thermodesorption (TDS) and analysis using gaschromatography (GC) / mass spectroscopy (MS) or GC / flame ionisation detection (FID) is described in DIN ISO 16000-6 [38]. Both specifications complement each other and enable the determination of VOC emissions from materials, such as building products, but also from electronic devices. These include computers, printers and copiers, the two latter ones also called hardcopy devices [66], [3].

Many products, which contribute to the avoidance of substantial environmental and health problems, can already be marked with the environmental symbol (RAL - UZ), generally known as "Blue Angel". The use of the label is voluntary and must be applied with RAL, German Institute for Quality Assurance and Marking (Deutsches Institut für Gütesicherung und Kennzeichnung e. V.). Adherence to specific criteria has to be proved.

A limitation of material emissions, in particular volatile organic compounds, is already identified in several environmental symbols. To be mentioned are RAL-UZ 38 for low-emission products of wood and timber materials [44], RAL-UZ 76 for low-emission timber material boards [47], RAL-UZ 12 a for low-pollution lacquers [43], RAL-UZ 102 for low-emission wall paints [42] and a new planned environmental symbol for low-emission floor covering adhesives and other products for flooring installation.

There are environmental symbol criteria available for office printers and copiers. RAL-UZ 85 [50] applies to printers, RAL-UZ 62 [46] to copiers and RAL-UZ 95 [51] to fax machines. The current criteria, valid since 1998 will run to the end of 2003. The evaluation criteria already include requirements for emission behaviour, however they only concern dust, ozone and styrene.

Current requirements were to be examined and VOC emission was especially to be included into the criteria, in addition to styrene emission. Also, characterisation was to be performed using emission rates of the devices instead of indoor air concentrations which build up gradually. This idea of characterisation of the devices around emission rates also forms the basis of the ECMA standard 328 published by ECMA (European Computer Manufacturer Association) in 2001 [18].

The necessity for a standardised test method for the determination of emission behaviour of hardcopy devices resulted among other things from the current publicly led discussion over the emission behaviour of these devices [39], [40], [4], [5], [65], [63]. Published measurement results were often not comparable since tests were performed using different procedures.

A suitable test method should be developed within the framework of the revision of the criteria for the environmental symbol for printers and copiers as well as the creation of the new environmental symbol for multi-functional devices, which enables identification of the potential for emission reduction. ENV 13419-1 [21] which is a test chamber standard and ISO 16000-6 [38] which describes the air sampling and analysis procedure and the ECMA Standard 328 [18] represented the starting points.

The test chamber procedure described in ENV 13419-1 [21] was originally developed for the determination of the emissions of volatile organic compounds from building products. These, as with other indoor-relevant materials, are usually examined for their emission behaviour over 28 days.

However, a considerably shorter investigation period is only available for hardcopy devices due to the limited supply of operational materials, in particular paper. It is in order of magnitude from a few minutes up to maximum one or two hours. Whether it is possible to achieve a reliable determination of VOC, dust and ozone emission rates within this short period, was a basic question to be answered within this project.

A test method should be developed on the basis of the investigations carried out and in agreement with the project-advisory working group. The investigations were to be supplemented by a cooperative test and comparative measurements.

Altogether ten different printers and copiers were available for the investigation and data acquisition, out of which four were selected for the cooperative test after the first emission data had become available.

Further questions to be answered concerned the contribution of operational materials such as toner and paper on the emission behaviour of the overall system.

2.2 Indoor air quality

The topic of indoor air quality has been pursued with increasing attention for many years. The Federal Government has recognized the importance of the relevant questions and dealt with them in the "Concept of the Federal Government for the improvement of indoor air quality" in 1992 [32]. Here a procedure which prevents or limits emissions has priority. In view of this the Federal Government prioritises its approach in such a way that an effective policy aimed at maintaining indoor air quality must concentrate on eliminating pollutant sources, or at least to sustainable reduce their emissions.

However, assessment values for the indoor air concentration are available only to a limited extent. Table 1 shows the indoor air pollutants for which guideline values have been established so far, analogous to the flow chart in accordance with [1]. Distinction has to be made here between a guideline value I, the so-called remediation target value and a guideline value II, the so-called action value. If guideline value I is adhered to, no impairment to health must be expected during a lifelong exposure provided no other substances interfere. Guideline value II represents an action-related toxicologically founded value which, if exceeded, require immediate countermeasures.

Table 1: Guideline values for indoor air in accordance with [1]; $^{*)}$ 8h mean value, $^{**)}$ half-hour value, $^{***)}$ weekly value

Substance	Guideline value I (Remediation target value)	Guideline value II (Action value)
Toluene [60]	0.3 mgm^{-3}	3 mgm^{-3}
Pentachlorophenol [2]	0.1 μgm^{-3}	1 μgm^{-3}
Dichloromethane [68]	0.2 mgm^{-3}	2 mgm^{-3}
Carbon monoxide [19]	1.5 $mgm^{-3*)}$ 6.0 $mgm^{-3**)}$	15 $mgm^{-3*)}$ 60 $mgm^{-3**)}$
Nitrogen oxide [20]	- -	60 $\mu gm^{-3***)}$ 350 $\mu gm^{-3**)}$
Styrene [59]	0.03 mgm^{-3}	0.3 mgm^{-3}
Mercury [34]	0.035 μgm^{-3}	0.35 μgm^{-3}
TCEP [58]	0.05 mgm^{-3}	0.005 mgm^{-3}
Bicyclic terpenes [57]	0.2 mgm^{-3}	2 mgm^{-3}

Evaluation criteria for indoor air quality were established by the Commission Indoor Air Hygiene (IRK) based on the sum of volatile organic compounds (TVOC) in order to account for the fact that interior air contains a multiplicity of organic compounds and that health complaints are often raised even though individual indoor air pollution conforms to current guideline values. It must be emphasised however that these TVOC values were not derived in accordance with the flow chart. To illuminate the uncertainties, concentration ranges are indicated instead of individual numerical values.

Based on this, a residence time of less than a day is expected in areas with TVOC concentrations between 10 and 25 mg m^{-3}. Such high concentrations may occur in the case of renovations. A TVOC value of 1 to 3 mg m^{-3} should not be exceeded in rooms destined for lengthier residence times over the longer term. An indoor TVOC concentration of 0.2 to 0.3 mg m^{-3} or if possible, lower, should be the average long-term aim to be achieved [31].

In addition, recommended guideline and limiting values are available which are displayed in Table 2.

Table 2: Recommended, guideline and limiting values for indoor air as per [41]

Substance	Recommended/Guideline /Limiting value	Publication
Formaldehyde	0.1 ppm (0.12 mg m^{-3})	Federal Health Institute 1977
Tetrachloroethene (Per)	0.1 mg m^{-3} (7-day mean value)	2. Federal Emission Prevention Ordinance (BImSchV)
Radon	250 Bq m^{-3}	Radiation Prevention Committee
Polychlorinated biphenyls (PCB)	3000 ng m^{-3} (action value) 300 ng m^{-3} (remediation target value)	Federal Health Institute
Carbon dioxide	0.15 % by volume	DIN 1946

Because toxicologically based data are missing for the concentration range of interest, assessment values can only be obtained, if at all, with great uncertainty for the majority of compounds that occur indoors or can be emitted from products.

For the evaluation of indoor air quality two further approaches have to be mentioned, those of Mølhave [36], [37] and Seifert [61], [62] which are also based on the Total

Volatile Organic Compounds (TVOC) concept. Table 3 displays the TVOC concentration ranges and the corresponding irritations and complaints and exposure ranges determined in accordance with [37].

Table 3: Dose vs. effect relationship for complaints due to exposure to solvent-like volatile organic compounds acting as air pollutants in non industrial interiors, in accordance with [37]

TVOC concentration [mg m^{-3}]	Irritations and complaints	Range of exposure
< 0.20	No irritations or complaints	Range of comfort
0.20 - 3.0	Irritations and complaints possible, under further exposures	Field of multiple exposures
3.0 – 25	Effect of the exposure and possible headache under further exposures	Range of complaints
> 25 *)	Headache, in addition neurotoxic effects may occur	Range of toxic exposures

*) Discussed in the study to a limited extent only, use with caution

Table 4 shows guideline values proposed by [61] for the TVOC concentration and VOC compound classes. It has to be emphasized that these values refer to long-term indoor air pollution. They are toxicologically unfounded [61] and may, in the case of ‘freshly introduced’ emission sources, be exceeded by a factor of 50 (for an age up to a week) to a factor of 10 (for an age of 6 weeks).

Reference [62] suggests that the concentration guideline values indicated in Table 4 for the individual compound classes should not be used in today’s situation any longer, as the VOC spectrum in indoor air has changed since a few compounds, such as glycol ether and aldehydes not seen earlier, have emerged and the concentration of some compounds, such as halogenated hydrocarbons which were previously more important, has considerably decreased’.

Table 4: Proposition of guideline values for the TVOC concentration and VOC compound classes, in accordance with [61] and [62]

VOC compound class	**Concentration [µg m^{-3}]**
Alkanes	100
Aromatic hydrocarbons	50
Terpenes	30
Halogenated hydrocarbons	30
Esters	20
Carbonyl compounds (aldehydes and ketones), without formaldehyde	20
Others	50
Sum (TVOC)	300

The concentration of any single compound should be a maximum 50 % of the value indicated for its VOC class and a maximum 10 % of the TVOC concentration.

The ECA report No. 18 [14] unites the aspect of the single substance evaluation with the TVOC concept, which suggests LCI values (LCI: Lowest Concentration of Interest) for single substances that are in part well above the values that are capable of being derived from the above recommendations as per [36], [37], [61], [62]. However the aim of the ECA report is directed more towards the evaluation of new building products, such as solid floor coverings, rather than indoor air.

Following this ECA report, the Committee for the Health Evaluation of Building Products (AgBB) has developed the AgBB evaluation schema „Health-related Evaluation Procedure for VOC from Building Products” [6], which is illustrated in Figure 1.

For emission measurement from building products, investigations have to be performed in emission test chambers. The tests are carried out after three and 28 days. After three days the sum of all detected carcinogens may not be greater than 10 µg m^{-3} and the TVOC value may not exceed 10 mg m^{-3}. For a classification ’recommended’ the TVOC value must be smaller than 1 mg m^{-3}.

After 28 days the sum of all detected carcinogens may not be greater than 1 µg m^{-3} and the TVOC value may not exceed 1 mg m^{-3}. For a classification ’recommended’ the TVOC value must be smaller than 0.2 mg m^{-3}. In addition, there is a limit for SVOCs: the sum of SVOCs may reach 0.1 mg m^{-3} at the most, for the category

’recommended’ only 0.02 mg m^{-3}. Furthermore, an individual material evaluation by means of the ’Lowest Concentration of Interest (LCI) values’ is performed.

Unlike the old flow chart shown in Figure 1, the current flow chart does not envisage any subdivision in ’recommended’ or ’fit for use’, it indicates only the category ’fit for use’.

The test results enable a comparison of emissions of individual materials under the standard conditions of the emission test chambers and the proof of possibly emitted carcinogenic substances or those suspected for causing cancer. However concentrations that occur in real indoor living space are affected by the combination of materials. In addition to real climatic and air exchange rate conditions and actual emitting surfaces, sorption of VOCs and SVOCs by other furnishing materials or house dust also plays a role.

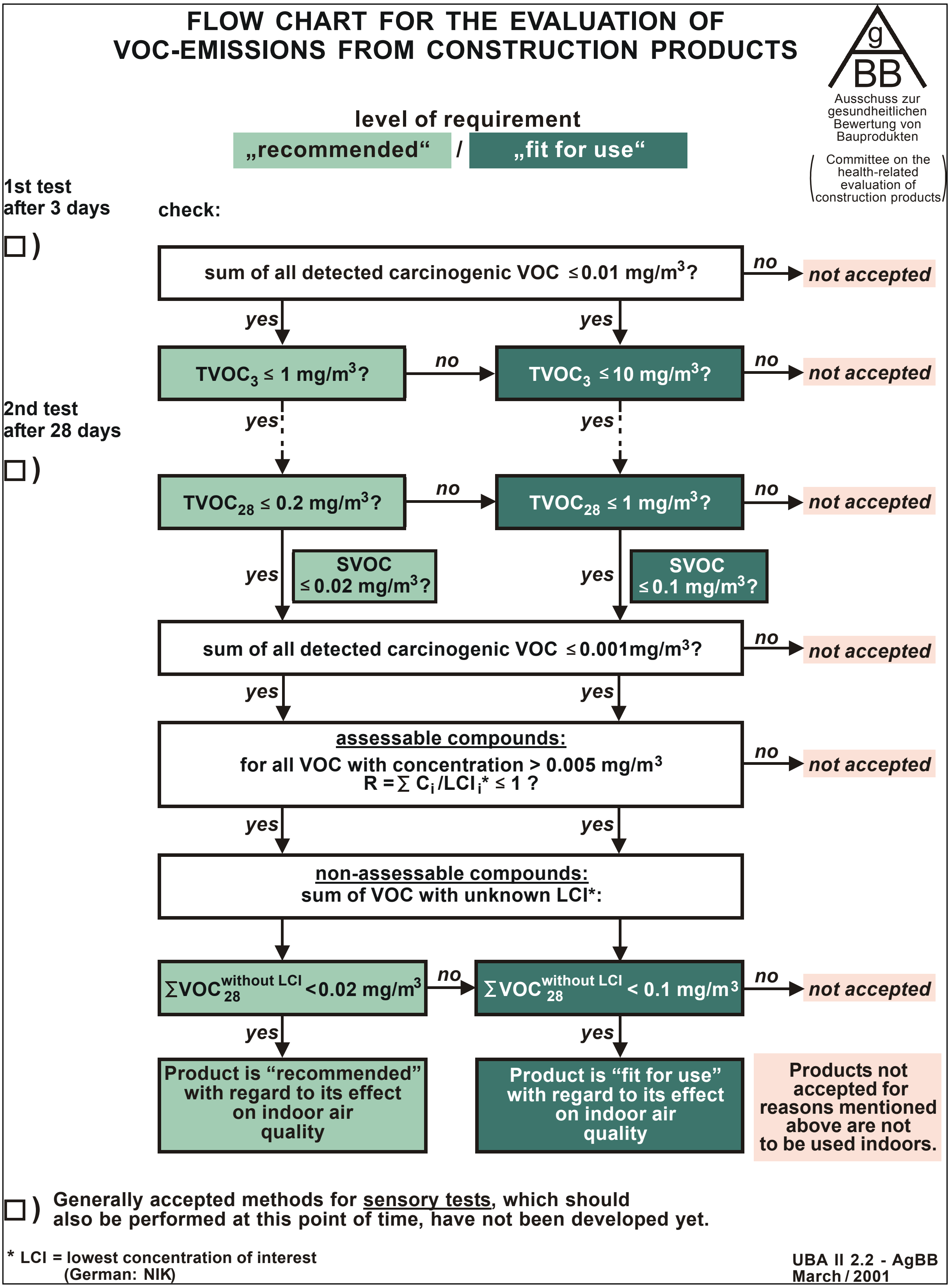


Figure 1: AgBB – Flow chart [6]

Various definitions exist for volatile organic compounds. Based on the definition in accordance with WHO or the ECA report Nr. 19 [15] distinction is made between volatility classes, splitting them into very volatile organic compounds (VVOC, boiling range <0°C to 50-100°C), volatile organic compounds (VOC, boiling range 50-100°C to 240-260°C), semivolatile organic compounds (SVOC, boiling range 240-260°C to 380-400°C) and semivolatile organic compounds predominantly occurring associated with particulate matter or as particulate organic matter (POM, boiling range greater than 380°C).

This differentiation into volatility classes is also included in the draft of DIN ISO 16000-6 [38] (Determination of VOC in indoor air and in test chambers) of September 2002. TVOC is defined as the sum of the concentrations of identified and unidentified volatile organic compounds eluted between and including n-hexane and n-hexadecane. A non polar capillary column is prescribed here.

In this report, analogous to DIN ISO 16000-6 [38], the term TVOC is understood to be the sum of the concentrations of all identified and unidentified substances eluted between n-hexane and n-hexadecane. Here however all identified compounds are individually quantified. The unidentified compounds are quantified using the response factor of toluene.

Organic compounds with a boiling point above 287°C, which correspond to that of n-hexadecane, are defined as semivolatile organic compounds (SVOC) analogous to DIN ISO 16000-6 in the draft of November 2000 [25].

2.3 Existing test specifications for the determination of emissions from hardcopy devices

a) Current assignment criteria for printers (RAL-UZ 85 [50]), copiers (RAL-UZ 62 [46]) and fax machines (RAL-UZ 95 [51])

Currently valid assignment principles only address requirements concerning dust, ozone and styrene emissions. Except for styrene, VOC emissions are not limited.

Emission tests must be performed in a 50m³ chamber. The starting temperature is 25 C ± 2 K and the relative humidity 50 % ± 2 %. Air sampling takes place at head height. The teflon-lined 50m³ chamber currently specified in the environmental label criteria, which is equipped with a non-textile floor covering, does no longer meet today's attested requirements on emission test chambers as per ENV 13419 - 1 [21].

The existing test provision does not contain further definitions for the air exchange rate in the chamber and for area or unit-specific air flow rates. The background concentration of the chamber and the chamber blank value is not limited. The period between the two collection periods of one hour each is not defined. Additional paper supply and removal, which must take place about every half hour due to the high printing capacity of modern devices, must be accomplished without people entering or remaining in the chamber. "Dr. Grauert's letter" is used as printer pattern.

b) ECMA Standard 328 "Detection and measurement of chemical emissions from electronic equipment" [18]

By issuing Standard 328 [18] the European Computers Manufacturer Association (ECMA) made an important step towards an efficient testing method for the determination of emissions from electronic devices. This method is based on dynamic emission chamber tests combined with efficient analyses. It is however too strongly focussed on electronic devices and hardly considers the specialities of tests on hardcopy devices which are operated with expendable material, and for short printing periods in particular. This led in the past to the fact that considerably different procedures were practiced with the consequence that emission data were sometimes difficult to compare and interpret. For example these were based on the presence of people in the test chambers or opening the test chambers for paper feed. Also, sampling points and procedures and calculation methods from emission rates differed e.g. between small and large emission test chambers. Permitted emission values were not formulated in the ECMA Standard 328, as a pure test standard.

2.4 Theoretical considerations

Emission measurements on materials or products are usually performed in emission test chambers over a longer period. The standard testing period for VOC emissions from building products amounts to 28 days [6], [21]. A decay in the VOC concentrations is usually observed during this time, as shown in Figure 2 by the example of concentration vs. time profiles of various terpenes emitted from a wooden material board [30]

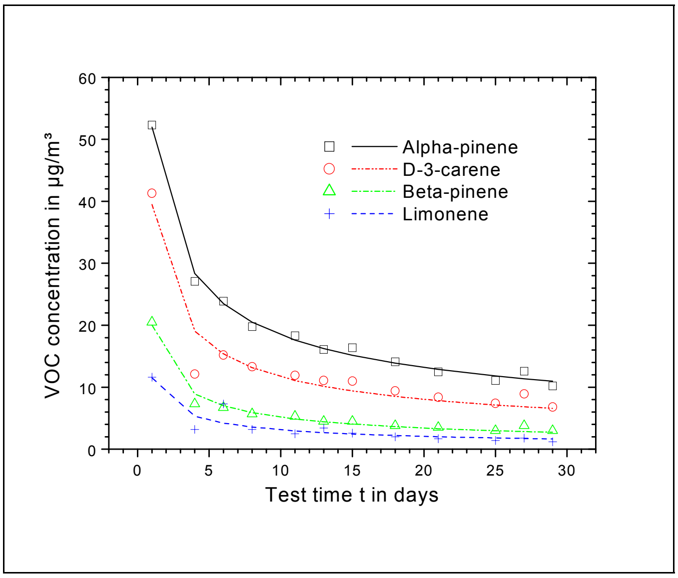


Figure 2: VOC concentration vs. time by the example of terpenes from a wooden material board

This concentration decay is due to an aging of the test material, which results in a VOC depletion in the outside material boundary layer. Consequently, emission processes are controlled by diffusion. A concentration rise within a few minutes to a few hours depends on chamber and/or cell volume and air exchange rate. It is however of secondary importance for these long-term tests, and is usually not detected by the instruments.

The investigations to be performed on hardcopy devices however allowed only 36 minutes at the most for the tests in the printing modus even with a maximum paper supply of 500 sheets for standard desktop devices. The question therefore was whether suitable dynamic test conditions, such as chamber volume and air exchange rate would reach a constant equilibrium concentration within this short period of time. Having the equilibrium concentration, the emission rate can be calculated directly from Equation 1, see [21].

$$\boxed{SER_u = c * n * V} \qquad \text{Equation 1}$$

c:	Analyte concentration in the test chamber	[µg m^{-3}]
SER_u:	Emission rate of analytes	[µg unit^{-1} h^{-1}]
n:	Air exchange rate	[h^{-1}]
V:	Test chamber volume	[m³]

The material concentration in an emission test chamber or a room considered sink-free for simplification's sake decays as a function of room volume, air exchange and emission rate over the time (see Equation 2).

$$\boxed{c = \frac{SER_u * (1 - e^{-n*t})}{V * n}} \qquad \text{Equation 2}$$

An assumed emission rate of SER_u = 1 mg h^{-1} provides the theoretical concentration profiles illustrated in Figure 3 for a 1m³ chamber.

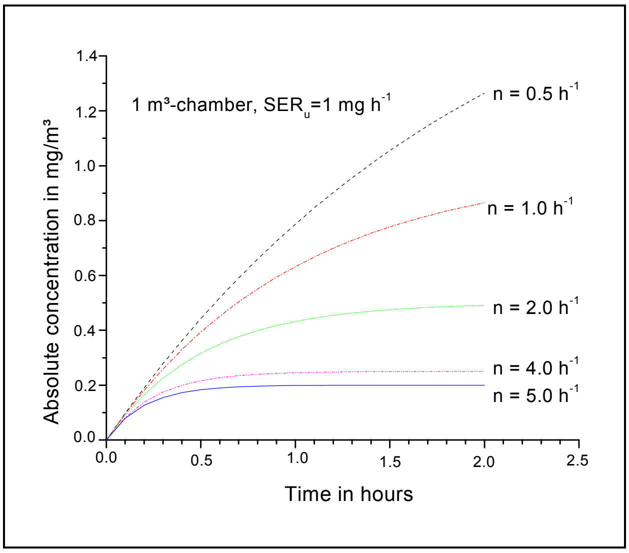


Figure 3: Theoretical concentration profiles in a 1m³ chamber with various air exchange rates (the emission rate of SER_u = 1 mg h^{-1} has been assumed for calculation purposes)

The concentration profiles are the same for a 20m³ chamber, but substantially lower concentrations were measured due to the larger chamber volume. This behaviour is shown in Figure 4.

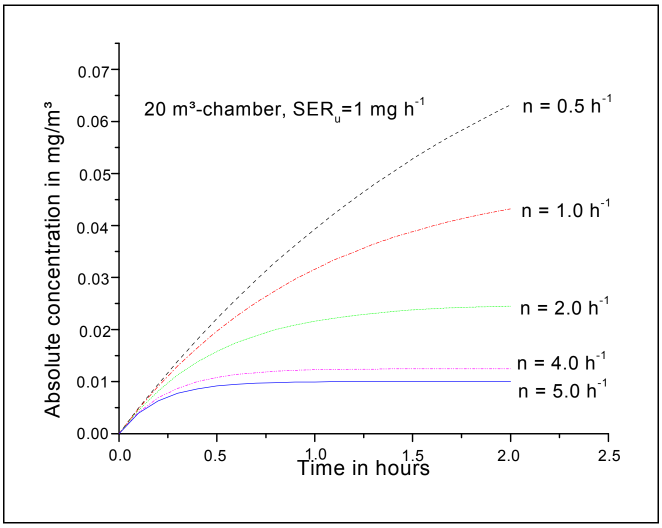


Figure 4: Theoretical concentration profiles in a 20m³ chamber with various air exchange rates (the emission rate of SER_u = 1 mg h^{-1} has been assumed for calculation purposes)

A plot of concentration profiles in percents of equilibrium concentration results in the concentration curves shown in Figure 5 which are identical for all chamber volumes.

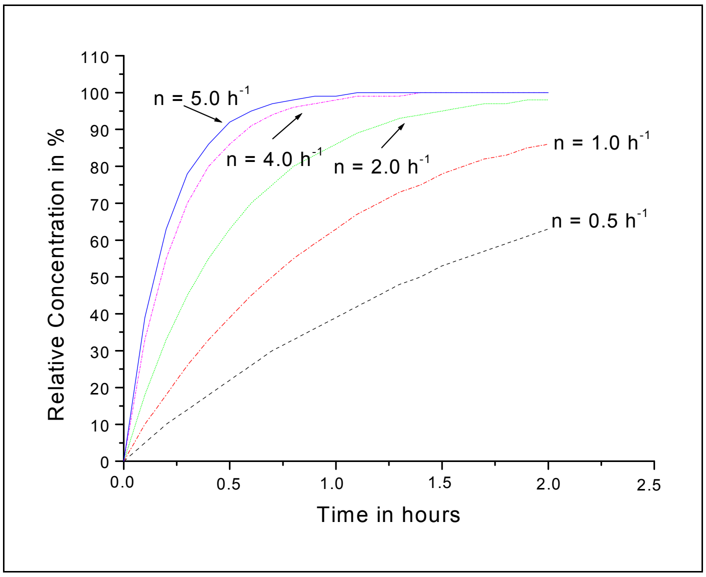


Figure 5: Theoretical percent concentration profiles for various air exchange rates (the emission rate of SER_u = 1 mg h^{-1} has been assumed for calculation purposes)

It can be seen that with large air exchange rates, e.g. n = 5.0 h^{-1}, equilibrium concentration 92% is almost reached within 30 minutes. With small air exchange rates, e.g. n = 0.5 h^{-1}, the concentration is only 22% of equilibrium concentration. It can be concluded from this that with short printing times of devices, greater air exchange rates are needed in order to reach equilibrium concentration within this short time. Only then is it permissible to calculate emission rates directly from the concentration.

Alternatively, when equilibrium concentration has not been reached, it is in principle possible to correct the emission rate with the help of an exponential function. Emission rates can then be calculated by Equation 3.

$$\boxed{SER_u = \frac{c * n * V}{1 - e^{-n*t}}}$$ Equation 3

Another alternative way to determine emission rates is by performing a continuous sampling from the beginning of the printing phase to the end of a follow-up phase. The concentration profile is then characterized, as shown in Figure 6**,** by a concentration increase analogous to Equation 2. The follow-up phase starts immediately after printing end with an analyte concentration c_0. The concentration decline from c_0 during the follow-up phase is described by Equation 4.

$$\boxed{c = c_0 * e^{-n*t}}$$ Equation 4

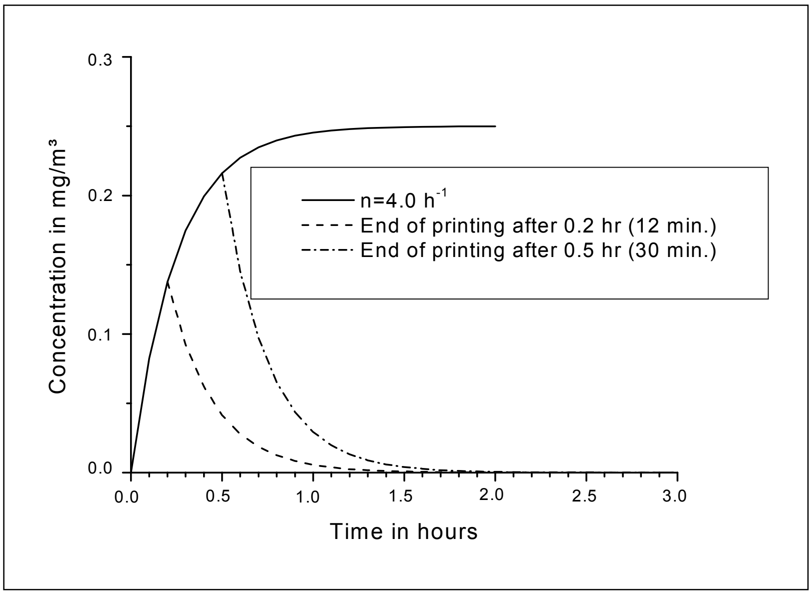


Figure 6: Theoretical concentration profile with an air exchange rate of $n = 4\ h^{-1}$ and a printing end in 0.2 and 0.5 hours

The above remarks refer in particular to the build-up of VOC concentrations. For ozone a special situation results, since apart from air exchange rate ozone degradation also plays a substantial role.

Emission rate is preferably determined via measurement from the beginning of the printing phase until the end of the follow-up phase for the determination of dust concentration using the gravimetric method.

3 Methods / devices

3.1 Emission test chambers

Emission test chambers enable the reproducible measurement of substances emitted from a material into the air under standardised and to a large extent constant test conditions.

The standard ENV 13419, Part 1 - 3, [21], [22], [23] drafted by CEN TC 264, WG 7 includes the determination of VOC emissions using emission test chambers and cells and, in addition, describes extraction, treatment and preparation of emission samples.

In Germany, 1m³ emission test chambers are frequently used for emission tests. A 1m³ commercial VOC emission test chamber has also been available for several years [35]. A temperature of 23 °C and a relative humidity of 50 % have been specified as climatic parameters.

Further important criteria, such as air exchange rate (n) and product loading factor (L), and the ratio of air exchange rate to product loading factor called area-specific air flow rate [21], [22] have been defined differently. The term unit-specific air exchange rate has been introduced for devices, since the determination of the surface of complex devices is impractical.

As far as air flow velocity is concerned, a range of 0.1 - 0.3 m s^{-1} [21] has been defined. The distance from the specimen surface for the measurement of air flow velocity has been defined as 10 mm [21].

In order to determine the emission behaviour of volatile organic compounds in small concentrations down to the lower µg m^{-3} range, not only must the usual parameters such as temperature, relative humidity, air exchange rate and air flow velocity be kept constant at specific values, but the test chambers must also satisfy a number of further special requirements. In particular:

- Inert chamber walls of glass or polished high-grade steel to minimize wall effects
- Efficient air mixing
- Minimise sealing materials capable of causing intrinsic emissions and adsorption and desorption effects
- Ability to clean the chamber, for example through firing
- Clean air and water supply with low VOC and dust content

The reason for choosing extremely inert chamber wall materials is to keep adsorption effects near the chamber walls to a minimum so that pollutant concentration in the air is not influenced by so-called wall effects. In addition to influencing pollutant concentration in the air during emission measurements, wall effects can impair subsequent investigations in the form of memory effects from the preceding measurements. A blank run is also necessary between two chamber tests and adequate desorption should be enabled for organic compounds that may have been adsorbed on the chamber walls.

In the case of semivolatile compounds in the range of SVOC/POM (cf. Chapter 2.2) wall effects may have serious impairing effects [28]. Memory effects can be tackled by firing at high temperatures for instance. Table 5 displays maximum background i.e. blank values – as per ECMA - Standard 328 [18] and ENV 13419, Part 1 [21] concerning TVOC, individual VOC, ozone and dust.

Table 5: Overview of the maximum tolerated background values of the emission test chambers as per [18] and [21]

Analyte	Maximum background concentration [µg m^{-3}] as per	
	ECMA Standard 328 [18]	ENV 13419, Part 1 [21]
VOC	< 2.0	< 2.0
TVOC	< 50	< 10
Ozone	< 4	No data
Dust	< 10	No data

Investigations within the framework of this project used 1m³ and 20m³ emission chambers with the same standard environmental conditions (T = 23 °C and 50 % relative humidity) being applied throughout. In addition, all chambers were operated with the same air flow velocity of 0.1 – 0.3 m s^{-1} measured at an emission surface with a distance of approx. 10 mm to the mid point of the hot wire anemometer.

Furthermore all test chambers were equipped with the same clean air supply system. Clean air was provided by a compressor in which a downstream cleaning unit removed oil, moisture, VOC and dust from the compressed air. The cleaning unit (Ultrafilter Oilfreepac) consists of a pre-filter (dust and aerosol separation), air drying (heatless dryer - silica gel with automatic regeneration), charcoal cartridge for VOC absorption and a fine filter and an afterfilter (submicrofilter < 0.01 µm, degree of separation 99.99999 %) to restrain both fine dust from the ambient air and abraded charcoal particles.

Various humidification principles and equipment was used to achieve the necessary relative humidity: either a mixed humidification combining dry and moist partial currents, a condensation point humidifier or a steam humidifier.

Ultrapure water was used for humidification which was obtained from desalinated water. In the case of ≤ 1m³ chambers the water was sent through an aftercleaning unit (EASYpure UV D7402) for further desalination and removal of possible organic compounds. An overview of the parameters in the individual emission test chambers is given in Table 6.

Table 6: Parameters of the emission test chambers used

Parameter	Unit	$1m^3$ chamber	$20m^3$ chamber
Volume	m^3	1	20
Wall material		high-grade steel	
Temperature (T)	°C	23	
Relative humidity (R.H.)	%	50	
Air exchange rate (n)	h^{-1}	1 - 5	1 – 2
Air flow rate (V°)	$m^3\ h^{-1}$	1 - 5	20 – 40
Device-specific air flow rate (q)	$m^3\ unit^{-1}\ h^{-1}$	1 - 5	20 - 40
Air supply		Clean air	

3.1.1 1m³ chambers

A standard VOC emission test chamber from the firm Vötsch Industrietechnik GmbH was used as the 1m³ emission test chamber within the framework of this project, which has been commercially available for some time, and conforms to ENV 13419-1 [21] and extensively reported in the literature. This chamber to be referred to in the following as a type B 1m³ chamber is schematically illustrated in Figure 7.

This chamber has an interior test space of high-grade steel with a smooth surface hermetically sealed from the surroundings. This separation is achieved, among other things, by the magnetic clutch applied to the test space fan, which is driven from the outside. Air conditioning of the chamber is performed using a thermally regulated blanket and condensation point humidification. To clean the chamber a heating system is available which eliminates memory effects through thermal desorption at up to 240 °C. The surface of the walls and fittings, which in principle are capable of adsorption of semivolatile compounds, is approximately 7 m².

For air sampling some connection points are provided to which the user can connect sampling tubes with 6 to 14 mm outer diameters. Further 1/4 in threaded sampling connection points are available for special high-flow-rate sampling sleeves. Figure 8 clarifies the situation by a photograph of the type B 1m³ chamber used.

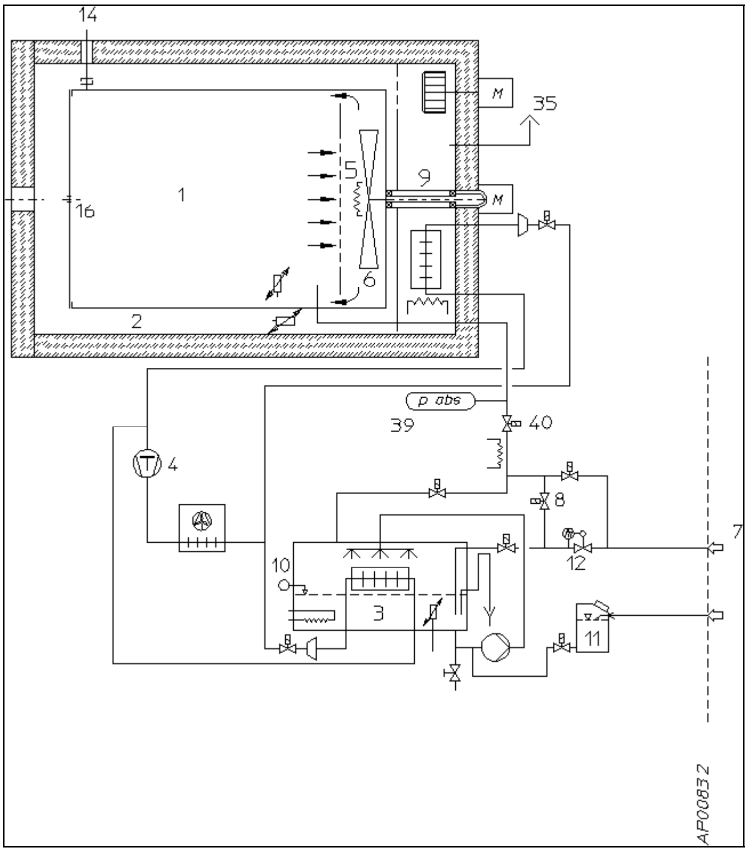


Figure 7: Schematic set-up of the standard 1m³ VOC emission test chamber (workshop drawing Voetsch Industrietechnik GmbH)

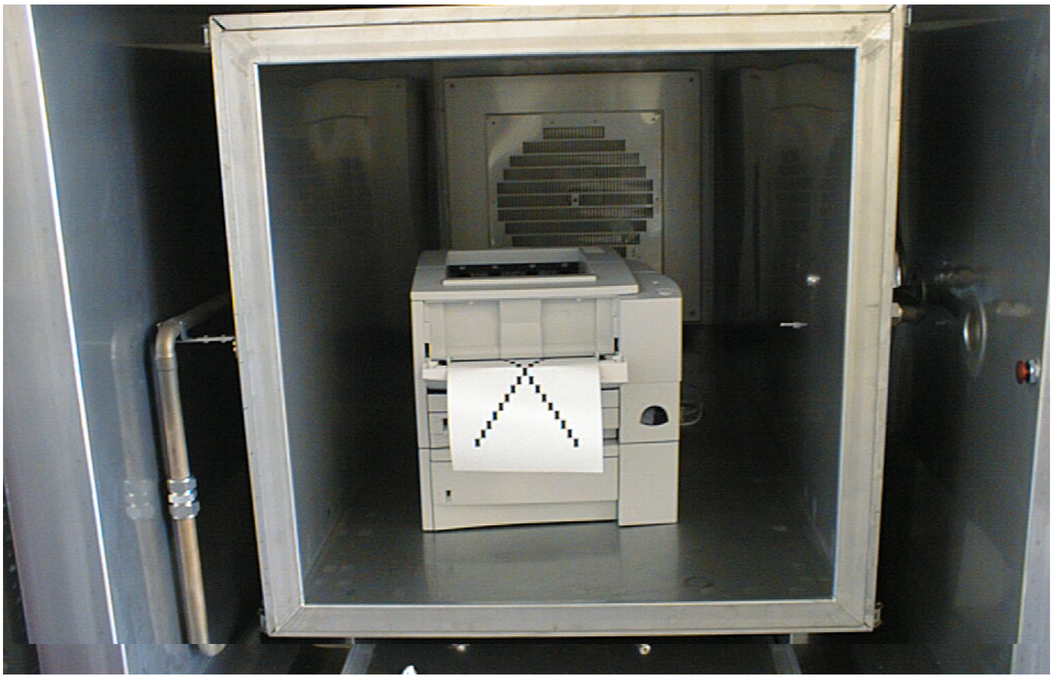


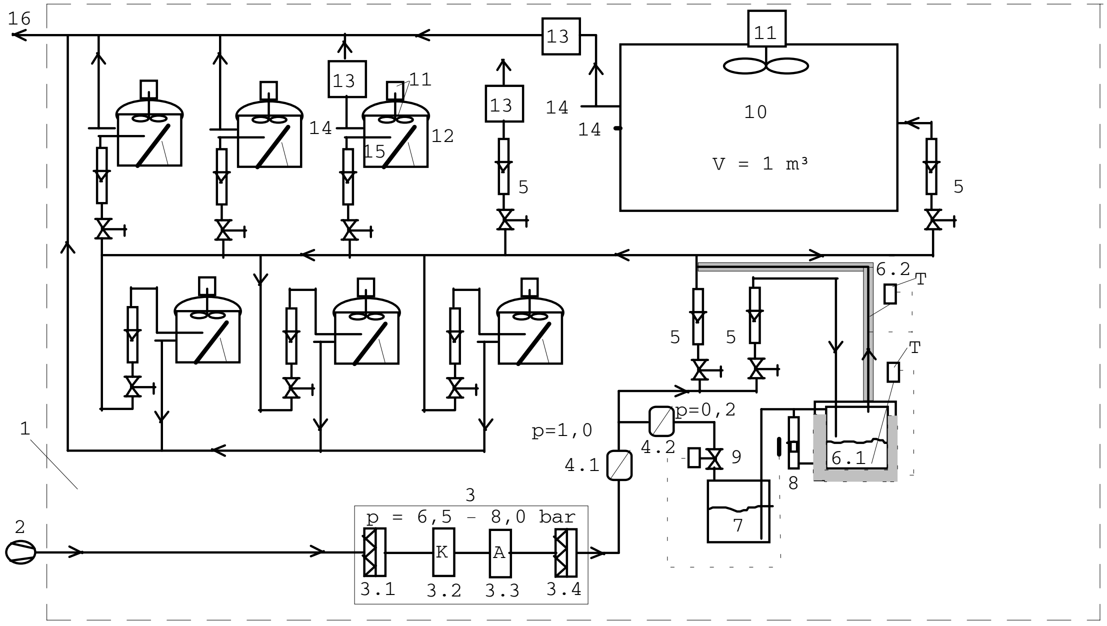
Figure 8: View of the type B 1m³ emission test chamber with a tested printer

A 1m³ chamber of electro polished high-grade steel was used as another chamber, which is part of a test chamber assembly and is shown in Figure 9 and Figure 10. The test chamber assembly consists, in addition to the 1m³ chamber, of several 0.02m³ chambers, which are all attached to the same supply system of air-conditioned clean air and are arranged in a climatic chamber. This 1m³ chamber will be called in the following a type A 1m³ chamber.

Figure 9: View of the type A 1m³ emission test chamber with a printer on test

By the arrangement in a temperature-controlled climatic chamber the principle of a thermally regulated blanket is likewise ensured. The 1m³ chamber is made of high-grade steel and is electro polished on the inside. The wall surface, including installations (fan, air deflector panels), amounts to approximately 7 m² as in the type B 1m³ chamber. The chamber is equipped with an air inlet and outlet port as well as several sampling points, furthermore a fan with an exterior speed-controlled motor for adjusting air flow velocity in the chamber. The door seal consists of a temperature-regulated emission free silicone profile. The air flow rate can be adjusted by a needle valve and flow meter to achieve the air exchange rate ($n = 0.5 - 4.7\ h^{-1}$).

Connection points are provided to which sampling tubes with 6 - 14 mm outer diameters can be connected for air sampling, likewise in the type B 1m³ chamber. Further ¼ in threaded sampling connection points are available for special high-flow-rate/high-volume sampling sleeves.



1	Climate chamber
2	Oil-free compressor
3	Air processing unit, consisting of
3.1	Filter unit (dust + aerosol)
3.2	Heatless dryer (τ ≈ -40 °C)
3.3	Activated charcoal
3.4	Submicrofilter (dust)
4.1	Pressure reducer 6.5 – 8.0 bar → 1.0 bar
4.2	Pressure reducer 1.0 bar → 0.2 bar
5	Gas flow meter and control
6.1	Temperature controlled water bath
6.2	Temperature controlled air supply pipe
7	Water storage flask
8	Level control, contact-free: magnet/reed contact
9	Electromagnetic valve
10	1m³ chamber (electro polished stainless steel
11	Fan
12	20 litre glass test chamber, based on DIN 12491 desiccator (6x)
13	Climate sensor
14	Air sampling point
15	Sample
16	Exhaust air outlet

Figure 10: Schematic set-up of small-chamber-arrangement (0.02m³ chambers) combined with a type A 1m³ chamber in the climate chamber

The chamber was operated with an air exchange rate of n = 1 h^{-1} for the tests. The air exchange rate was increased to n = 4.7 h^{-1} to ensure great air flow rates.

3.1.2 20m³ chamber

ECA Report Number 2 [16] describes the emission test chamber method for test chambers with a volume of $\geq$ 12 m³ to determine formaldehyde equilibrium concentration. DIN V ENV 717-1 also describes large chambers with a volume of

≥ 12 m^3 for the measurement of formaldehyde equilibrium concentration. Figure 11 illustrates a scheme of 20m^3 chambers used in the tests. Figure 12 explains the situation by a photograph of the 20 m^3 chamber used.

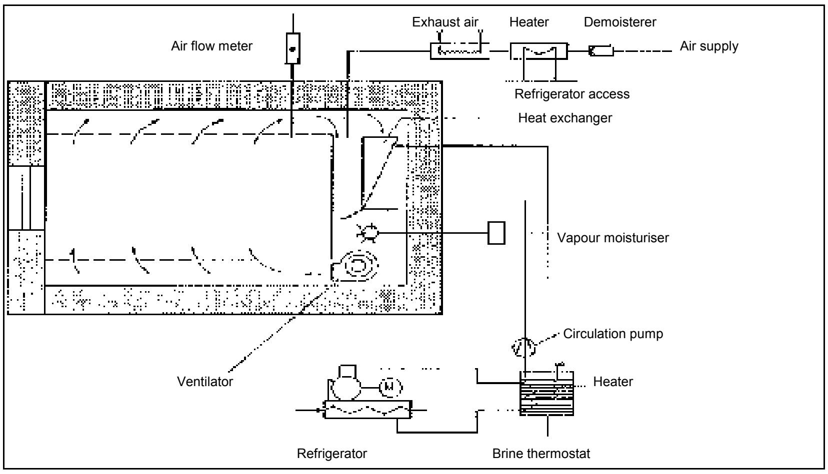


Figure 11: Scheme of 20 m^3 formaldehyde test chamber, SYSTEM WEISS

Figure 12: View of the 20m^3 emission test chamber with a printer on test

This chamber was connected to the same clean-air supply system used for the other chambers too. Chamber blank tests performed without the clean-air supply system provided unacceptably large, unstable blank values.

Since this chamber was originally conceived for formaldehyde measurements, it fails to correspond substantially to the requirements of VOC emission test chambers. In particular this concerns temperature control and air distribution devices. Instead of the recommended thermally regulated blanket, temperature adjustment is applied in the 20m³ chamber by a large-area heat exchanger through which air is kept in circulation (Figure 11). Surfaces introduced by heat exchangers may have undesired adsorption effects on the internal surfaces within the chamber. The extent to which measurement results are affected was examined in this report using comparative measurements including other chambers (cf. Section 6.5) .

The advantage of a large chamber is that complex material combinations and/or large freestanding hardcopy devices can also be tested. The 20m³ chamber is usually operated with an air exchange rate of $n = 1\ h^{-1}$ i.e. a volumetric air flow rate of $20\ m^3\ h^{-1}$.

3.2 Climate

Climate measurements were carried out on the basis of calibrated devices. Climate sensors combined with a data logger of Type 3290-8 of the ALMEMO company were used as external measuring instruments. This enabled a continuous measurement at different measuring points. Calibration of the individual sensors took place with the help of measurements using the Aßmann aspiration psychrometer and a calibrated thermometer.

Measurement accuracy of climate sensors

Moisture sensor	:	Type FH A 646-R
Range of measurement	:	5% to 98% R. H.
Maximum linearity deviation	:	± 2% R. H.
Operational temperature	:	– 30 °C to +100 °C
Nominal temperature	:	25 °C ± 3 K

Temperature sensor : NTC Type N
Accuracy : 0 °C to 70 °C ± 0.1 K
Air pressure sensor : Type FD A 612 MA
Range of measurement : 0 mbar to 1050 mbar
Accuracy : ± 0.5% (typical ± 0.1% of end value)
Operational temperature : 25 °C ± 3 K

3.3 Dust

The gravimetric method was used as a conventional method for the determination of dust emission rate. Additionally a particle counter was used to determine particle numbers.

3.3.1 Particle count

A particle counter of Type 1.100 of Grimm Labortechnik GmbH was used as shown in Figure of the Appendix. The equipment uses the scattered light principle and a laser diode serves as a light source. The measurement data are recorded online from the start of the printing phase until the end of the follow-up phase and transferred in real time over an interface to a PC. Evaluation is performed through a table calculation programme using an algorithm developed by the authors.

Dust-containing air was sucked into the measuring chamber of the particle counter with the help of a built-in pump in such a way that the scattered light generated can be measured with the help of a pin diode in an angle of 60° to 120°. A pulse height analyzer classifies scattered light signals and assigns the detected particles automatically to the four particle size classes < 0,1 to 1, 1 to 2, 2 to 5 and 5 to 10 µm. Measuring data are indicated in 10 time periods per minute, 5 seconds each , then an alignment and a zero measurement are carried out for 10 seconds.

Calculation of particle emission rate

All four particle size classes tested that were summed up to calculate the particle concentration in the test chamber were considered when calculating the particle emission rates.

$$\boxed{SER_{u_P} = \frac{\hat{c}_P * n * V * t_T}{t_{\mathrm{Pr}}}} \qquad \text{Equation 5}$$

$$\boxed{\hat{c}_P = R\int_0^{t_T} c_P dt} \qquad \text{Equation 6}$$

$$\boxed{R = \frac{1}{1000 * t_T}}$$ Equation 7

c_P^*:	Particle concentration in test chamber (from < 0.1 µm to 10 µm)	[particle* litre^{-1}]
$\hat{c}_P$ *:	Medium particle concentration in test chamber over the total sampling time	[particle* litre^{-1}]
$SER_{u\,P}^*$:	Medium particle emission rate	[particle unit^{-1} h^{-1}]
n:	Air exchange rate	[h^{-1}]
R:	Proportionality factor	[min^{-1}]
t_{Pr}:	Net printing or copying time	[min]
t_T:	Total sampling time	[min]
V:	Test chamber volume	[m³]

*Particle concentrations and medium particle emission rate refer to size interval of 0.1 to 10 µm particle diameter

Quality assurance

The device was calibrated by the manufacturer and the calibration will be repeated within appropriate periods.

3.3.2 Gravimetry

The basis of the procedure is measuring the difference in weight of a glass-fibre filter, through which a defined air sampling volume from the emission test chamber has been passed, by means of an ultra micro scale (Type UMX2/M; manufacturer Mettler - Toledo). The ultra micro scale is shown in Figure in the Appendix.

Measurement procedure

Air sampling is carried out over a defined time interval (total printing and follow-up phase). Air taken from the test chamber during this time interval is transported by a pump (Müller; GSA 50) through a glass-fibre filter (Schleicher & Schuell, diameter 50 mm). The volume of air sucked through the filter is determined by a gas flow meter (Schlumberger, REMUS 4 G 1.6). The absolute dust mass weighed is obtained by the differential weight of the filter. The medium dust concentration in the test chamber can be determined from both values as per Equation 9 and from this the specific dust emission rate as per Equation 8.

Standard conditions of gravimetric dust measurement

Dust filter	Glass-fibre filter with container
Sampling point	In the middle of chamber wall for type A and B 1m³ chambers Direct in the chamber approx. 30 cm above the test object for the 20m³ chamber
Sampling flow rate	Up to maximum 90 % of air flow rate in the chamber during the sampling phase
Sampling time	Total printing and follow-up time

Calculation of dust concentration and emission rate

$$\boxed{SER_{u_D} = \frac{m_D * n * V * t_T}{V_P * t_T}} \quad \text{Equation 8}$$

$$\boxed{c_D = \frac{m_D}{V_P}} \quad \text{Equation 9}$$

c_D:	Dust concentration in the test chamber	[µg m^{-3}]
$SER_{u\,D}$:	Dust emission rate	[µg unit^{-1}h^{-1}]
m_D:	Weighed dust mass (climate-corrected)	[µg]
n:	Air exchange rate	[h^{-1}]
t_{Pr}:	Net printing and copying time	[min]
t_T:	Total sampling time	[min]
V:	Test chamber volume	[m³]
V_P:	Air volume sucked through glass-fibre filter	[m³]

Glass-fibre filters (measuring filters) used for gravimetric dust measurement must be stored before the measurement in an air-conditioned room (weighing room: temperature: 23°C ± 2 K; relative humidity: 50 % ± 5 %) and conditioned in the dominant climate there until the mass remains constant. Since even unavoidably small fluctuations of relative humidity in the weighing room affect the mass of glass-fibre filters, an empty glass-fibre filter (reference filter) is weighed simultaneously to the measuring filters before dust sampling (tare), in order to be able to minimize the influence of climate on the filter mass by a climatic correction.

During dust sampling in the climatic chamber, air is sucked through the measuring filter. Since the relative humidity of this air can deviate from that in the weighing room, the measuring filter must again be conditioned after dust sampling in the weighing room until the mass remains constant.

The reference filter will remain in the weighing room over the entire time and weighed again when dust weighing of the measuring filter (gross weighing) is performed. Mass difference between the first and second weighing, determined on the reference filter, is due to climatic changes and is subtracted from or added to the determined gross mass of the measuring filter.

Determining the absolute dust weight of the measuring filter (climate-corrected)

$$\boxed{m_D = (m_{MF_{gross}} - m_{MF_{tare}}) + (m_{RF_1} - m_{RF_2})} \qquad \text{Equation 10}$$

m_D:	Weighed dust mass (climate-corrected)	[µg]
$m_{MF\ gross}$:	Mass of conditioned measuring filter after dust sampling	[µg]
$m_{MF\ tare}$:	Mass of conditioned measuring filter before dust sampling	[µg]
$m_{RF\ 1}$:	Mass of conditioned reference filter simultaneous to weighing filter before dust sampling	[µg]
$m_{RF\ 2}$:	Mass of conditioned reference filter simultaneous to weighing filter after dust sampling	[µg]

Quality assurance

The scale was calibrated by German Calibration Services (Deutscher Kalibrierdienst, DKD) per DKD Guideline 7-1 for Calibration of Electronic Non-automated Scales and the calibration was repeated within appropriate periods. For a maximum load of 2.1 g and a readability of 0.0001 mg, standard deviation was determined with a load of 1 g amounted to 0.00039 mg.

Detection limit (DcL) and determination limit (DrL)

DcL and DrL were estimated by considering the measurement inaccuracy of the scale indicated by the manufacturer, assuming a complete climatic correction via the reference filters and a determined average mass of the empty glass-fibre filters of 140 ± 5 mg. Table 7 displays DcL and DrL of gravimetric dust measurement.

Table 7: DcL and DrL of gravimetric dust measurement

Test chamber	**Dust emission rate [mg h^{-1}]**	
	DcL [mg h^{-1}]	**DrL [mg h^{-1}]**
Type A and B 1m³ chamber	0.035	0.106
20m³ chamber	0.150	0.450

3.4 Ozone

A model 3010 ozone analyser of UPM was used to determine ozone concentration, shown in Figure in the Appendix. The basis of the measurement method is the flameless reaction of ozone with ethylene accompanied with chemiluminescence which can be recorded photometrically. Ozone concentration is continuously determined. In addition to taking notes manually, data recording is performed by electronic data acquisition. Three working modes can be distinguished:

a) 'Zeroing': ozone-free air enters the reactor. Chemiluminescence does not occur and zero point alignment can take place.
b) 'Calibrating': an ozone generator is operated which produces an ozone concentration of 0.160 ppm at the reactor. The calibration point is adjusted to match.
c) 'Measurement': after completing the two-point calibration the measurement procedure can start. A permanent measurement signal is produced. The output voltage values are recorded electronically (data logger). A conversion factor between voltage, measurement range adjustment and standardisation curve in ppm values has to be considered here.

<u>Measurement procedure</u>

Ozone emission of printers and copiers was tested as follows:

a) Chamber blank valuation without any device tested
b) Determining the ozone concentration in the cold and standby phase
c) Ozone determination during printing and copying

Ozone determination for printing or copying started immediately with the beginning of the printing job and continued until the end of the follow-up phase. Concentration was recorded at least every 30 seconds. Ozone concentration was permanently recorded by an electronic data logger. The ozone half-life was determined from the decay curve in the follow-up phase. An initial approximation shows the same conditions still prevail at this time as during the printing job.

Ozone half-life is difficult to determine under test conditions for very small ozone emission rates. In order to make an evaluation possible nevertheless, after the printing job and the follow-up phase, ozone was injected into the chamber and the ozone half-life was determined. The chamber remained loaded and the printed paper remained likewise in the test room. Climate conditions, in particular air exchange rate, were the same as during the printing test. An initial approximation shows a reasonable ozone half-life could be determined under these conditions. Calculation can then be performed as per Equations 11 and 12.

Calculation of ozone emission rate

c_{max} and k' are the crucial variables for the determination of ozone emission rate and they are closely connected. If the ozone half-life is small, the attainable maximum ozone concentrations are also small, compared with those with larger ozone half-life. A direct statement on ozone emission rate through the maximum ozone concentration is therefore not possible. Equations 11 and 12 were used to calculate ozone emission rate taking account of ozone half-life:

$$\boxed{SER_u = \frac{c_{\max} * k' * V * p}{T * R}}$$

Equation 11

$$\boxed{k' = \frac{\ln 2}{H'}}$$

Equation 12

SER_u:	Ozone emission rate	[µg unit^{-1} h^{-1}]
c_{max}:	Maximum ozone concentration	[µg m^{-3}]
k':	Proportionality factor	[min^{-1}]
H':	Ozone half-life under test conditions	[min]
V:	Test chamber volume	[m³]
p:	Air pressure	[Pa]
T:	Absolute temperature	[K]
R:	Gas constant (339.8 [Pa K^{-1}] for ozone)	[Pa K^{-1}]

Quality assurance

First of all human reading error in the measuring ranges had to be reduced to a minimum to ensure the quality of ozone determination. Different ranges can be selected for the determinations. Accordingly, measurement errors depend on the selected measurement range and are about 2 % of the selected measurement range. A permanent recording of the measuring voltage values over two signal outputs (voltage signal/current signal) was used for data monitoring. Measurement range change-overs cause problems during evaluation so they were therefore separately recorded.

Detection limit (DcL) and determination limit (DrL)

DcL and DrL were estimated by considering measurement inaccuracy of the ozone analyser indicated by the manufacturer of a measurement under standard conditions. Table 8 shows DcL and DrL of the ozone measurement.

Table 8: DcL and DrL for ozone measurement

Test chamber	**Ozone emission rate [mg h^{-1}]**	
	DcL [mg h^{-1}]	**DrL [mg h^{-1}]**
Type A and B 1m³ chambers	0.006	0.018
20m³ chamber	0.033	0.099

3.5 VOC

VOC sampling from the test chamber air took place per DIN ISO 16000-6 [38]. The air sample was pulled on a glass tube filled with Tenax TA [178 mm tube length, OD 6 mm, ID 4 mm, 200 mg Tenax TA (60 - 80 mesh) secured with glass wool stuffing and glass wool stuffing /wire net on the side towards the pump]. Before sampling, the Tenax tubes were spiked using cyclodecane and deuterated toluene (d_8) as internal standards diluted in methanol (1 µl). The sample volume was 0.5 l (individual printing phases), 2 l (cold and standby phase) and 9 l (printing plus follow-up phase). The sampling flow rate amounted to 100 ml/min.

TDS was performed in a TDS system (Gerstel TDS-2) coupled with a cold feed system (Gerstel KAS-3) to cryofocus the thermodesorbed analytes. The temperature programme of the thermodesorption unit began at 40 °C with a heating rate of 40°C/minute up to 280°C. The final temperature of 280 °C was held for 5 minutes. Cryofocusing occurs at -150 °C, subsequent heating was carried out with a heating rate of 12°C/s up to 280°C.

Separation of the analytes extracted from the cold feed system was performed gaschromatographically (HP GC 5890 II) by means of a 30m column (HP-5 MS, 0.25 mm diameter, 1 µm layer thickness) or a 60m column (HP1-MS, 0.25 mm diameter, 0.25 µm layer thickness). An example of a temperature programme of gaschromatographic separation is shown in Figure 13. The GC / MS system is illustrated in Figure in the Appendix.

The identification and quantification was performed using a quadruple mass spectrometer as a detector (HP-MSD 5972). The scan range lay at 25 - 400 amu with 1.9 scans per sec at an interface temperature of 300°C. For substance identification the mass spectrum library NIST-98 was available. Using the described procedure, semivolatile compounds up to hexacosane can be quantitatively verified (C_{26} alkane, boiling point approx. 413°C) [29].

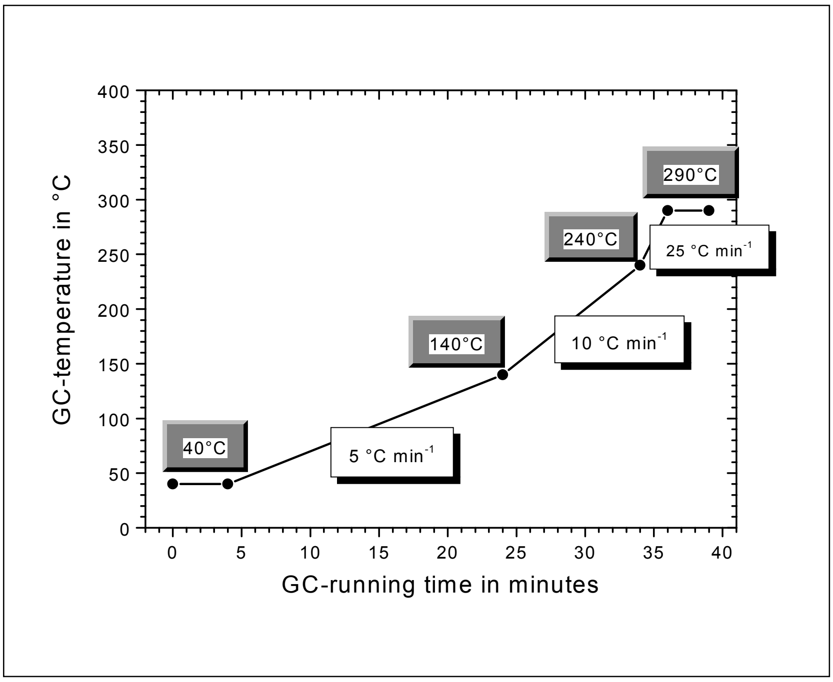


Figure 13: Temperature programme for gaschromatographic separation

Calculation of TVOC emission rate for the cold and standby phase

All substances were identified as far as possible and individually quantified using the relative response factors determined from a calibration by internal standard. For each measurement time, the sum of the concentrations of all parameters identified whose retention time was between n-hexane and n-hexadecane and had a concentration of $\geq$ 2 µg m^{-3} was calculated. If it was not possible to identify certain substances or determine their relative response factor, the quantification was performed on the assumption of the response factor of deuterated toluene.

The TVOC value was calculated as the sum of the concentrations of all identified and non-identified substances having a concentration of $\geq$ 2 µg m^{-3}, whose retention time was between n-hexane and n-hexadecane.

The emission rate during the cold and standby phase was calculated with the concentration from the sampling of the last twenty minutes of the two-hour phase using Equation 13.

$$\boxed{SER_u = c * n * V} \qquad \text{Equation 13}$$

$$\boxed{c = \frac{m_{VOC}}{V_S}} \qquad \text{Equation 14}$$

c:	VOC concentration during cold and standby phase	[µg m^{-3}]
SER$_u$:	VOC emission rate during cold and standby phase	[µg h^{-1}]
m$_{VOC}$:	analysed mass of VOC during cold and standby phase	[µg]
n:	Air exchange rate during cold and standby phase	[h^{-1}]
V:	Test chamber volume	[m³]
V$_S$:	Sample volume during cold and standby phase	[m³]

Calculation of TVOC emission rate for the printing phase

The emission rate during the printing phase can be calculated in two ways. These depend on the time of sampling:

a) From the continuous sample from the start of the printing phase to the end of the follow-up phase, the emission rate was calculated using Equation 15:

$$\boxed{SER_{u\,\mathrm{Pr}\,F} = \frac{m_{VOC_{\mathrm{Pr}\,F}} * n_{\mathrm{Pr}\,F} * V * t_T}{t_{\mathrm{Pr}} * V_S}} \qquad \text{Equation 15}$$

$SER_{u\,PrF}$:	VOC emission rate determined from printing and follow-up phase	[µg h^{-1}]
$m_{VOC\,PrF}$:	Analysed mass of VOC during printing and follow-up phase	[µg]
n_{PrF}:	Air exchange rate during printing and follow-up phase	[h^{-1}]
t_{Pr}:	Net printing or copying time	[min]
t_T:	Total sampling time	[min]
V:	Test chamber volume	[m³]
V_S:	Sample volume during printing and follow-up phase	[m³]

b) For the sampling until the end of the printing phase, the calculation used Equation 16, (cf. Section 2.4).

$$\boxed{SER_{u\,\mathrm{Pr}} = \frac{c_{\mathrm{Pr}} * V * n_{\mathrm{Pr}}}{1 - e^{-n_{\mathrm{Pr}} * t}}} \qquad \text{Equation 16}$$

c_{Pr}:	VOC concentration during printing phase	[µg m^{-3}]
$SER_{u\,Pr}$:	VOC emission rate determined from the printing phase	[µg h^{-1}]
n_{Pr}:	Air exchange rate during printing phase	[h^{-1}]
V:	Test chamber volume	[m³]
t:	Medium time of sampling [h], calculated from start of printing (e.g.: period of time of sampling minute 5 (t_1) to minute 10 (t_2); t = 0.5 × (t_1 + t_2) = 0.125 h (7.5 minutes))	

For the further sampling during the printing phase Equation 16 was used without the correction term in the denominator, which describes a temporal change in concentration up to achieving equilibrium. Emission rates calculated in such a way do not correspond to the real emission rates and are designated as apparent emission rates (SER*) in the following text.

Quality assurance

Quality assurance of sampling was performed by regular testing of the flow rate of the pumps used for the sampling. This was measured after charging the batteries of the pumps with the aid of a calibrated electronic flow meter (HP) and adjusted to 100 ± 1 ml/min.

Quality assurance of the analytical instrument (GC MS) was performed, in addition to multi-point calibrations of the compounds to be analysed, which were daily performed by measuring a standard solution and by adding the same amount of the internal standard on Tenax before sampling. Deviations in the quantification of the standard solution or the peak of the internal standard from the standard value indicated malfunction or changes in the instrument’s operation.

Checking the mass spectrometer tuning file offered a further control option. A tuning file report was compiled every day having the same parameters. Changes in signal intensity signalised changes in the mass spectrometer.

To be able to perform an exact quantification, a blank evaluation was carried out on an empty chamber before placing the device inside to guarantee that the substances found have in fact been emitted from the material tested. However, this blank value not only includes possible impurities from the test chamber but also impurities from the Tenax tube and the GC MS device. The Tenax tubes were therefore not stored longer than 72 h before sampling, otherwise a new 15-minute cleaning heating was performed in a helium flow at 280°C

The laboratory regularly participates in and organizes co-operative tests, such as VOCEM, BAM, GEV, to enhance quality assurance for the total procedure (test chamber method, sampling and TDS/GC-MS analysis).

Detection limit (DcL) and determination limit (DrL) for the printing and follow-up phase

Detection and determination limits depend among other things on the sample volume. The sample volume is about 9 litres (with 100 ml/min) when sampling is performed in a 1m³ chamber with an air exchange rate of 1 per hour from the beginning of the printing phase throughout to the end of the follow-up phase. When a sampling is performed six minutes before the end of the printing phase, the sample volume is 0.6 litres (with 100 ml / min).

Generally 1 ng of a VOC can be safely detected by GC/MS in scan modus. Detection and determination limits for single VOCs displayed in Table 9 were obtained from these tests for the emission rates.

Table 9: DcL and DrL of individual VOC tests

Test chamber	SER_{VOC}	VOC emission rate [mg h^{-1}]	
		DcL [mg h^{-1}]	DrL [mg h^{-1}]
A and B 1m³ chamber	SER_{VOC} measured in printing phase only	0.010	0.030
	SER_{VOC} measured in printing and follow-up phase	0.002	0.006
20 m³ chamber	SER_{VOC} measured in printing phase only	NTBP *	NTBP *
	SER_{VOC} measured in printing and follow-up phase	0.013	0.039

* NTBP: Not to be performed as per test procedure

3.6 Materials tests

3.6.1 Direct TDS of paper

The direct TDS method functions as far as device technique is concerned in a similar way to Tenax TDS. The main difference is that possible emissions from small material quantities are tested without the extra stage of air sampling from a test chamber. The material sample is thermodesorbed in the glass tube itself. Statements can be made for the material on possible out-gassing substances with the help of this screening before the test chamber measurement.

This method was applied for the sheets of paper used in the research project. For this purpose a strip of approx. 3 mm width and a mass of 20 mg was cut from a DIN A4 sheet. The resulting length of the strips was between 60 and 80 mm.

A strip was placed in a TDS glass tube for the direct TDS, which was then introduced by an autosampler into the TDS oven. The direct TDS was started at 40°C temperature and then increased at 40°C/min, until the final temperature of 180°C was reached. This was maintained for 5 minutes. The final temperature of 180°C was derived from some manufacturers' data on the temperature of the fixing unit during the printing process.

3.6.2 Headspace method for toner

2 g of the toner was weighed in a 20 ml flanged rimmed headspace glass for each test and a solution of the internal standard in methanol was added. The glasses were then covered with metallic flanged caps. Analysis was performed with a headspace auto sampler (Gerstel MPS) connected to a GC / MS combination (Agilent 6980/5973). The glasses were conditioned for two hours at 90 °C, then a gas volume of 500 µl was removed with a gas syringe (90°C) and injected directly in the GC. Calibration is performed by individual mass traces from the total ion chromatogram of the MS.

Volatile contents of the toners, such as toluene, xylene, ethylbenzene, styrene etc., were tested at low costs on the apparatus and clean-up using this method, which was made available by the State Institute for Trade in Nuremberg (Landesgewerbeanstalt, LGA) [33]. d_6 benzene and d_9 styrene served as internal standards. Calibration was made for benzene, toluene, ethylbenzene, o-, m- and p-xylene, i-propylbenzene, benzaldehyde and styrene.

Reproducibility of this method was tested by multiple determination of a toner and by loading specific standards on a toner and determining the analyte recovery rate. The reproductibility yielded a medium standard deviation of less than 7% for concentrations of 1 mg/kg and more, and a standard deviation of less than 13% for concentrations under 1 mg/kg for triple measurements of five different toners. However, one of the toners exhibited stronger fluctuations. The standard deviation of the average value was 20% for all concentrations between 2 and 25 mg/kg.

The analyte recovery rates of volatile components from toners were determined in such a way that a toner was selected, which exhibited only very low own emissions. A known quantity of standard solution was then added to this toner. Subsequently, the toner was treated and tested exactly like the other toner samples. The concentrations were compared with the empty headspace glass.

Table 10: Analyte recovery rate (ARR) [%] of compounds by comparing an empty headspace glass with a toner-filled glass

Compound	Benzene	Toluene	Ethylbenzene	p-Xylene	m-Xylene	o-Xylene	Cumene	n-Propylbenzene	Styrene	Benzaldehyde
ARR [%]	30.7	18.3	11.4	10.3	10.3	7.8	8.7	7.1	5.6	0.5

Table 10 shows analyte recovery rate of selected compounds compared with the same compounds measured in an empty glass. The toner values are average values from a quadruple measurement with a medium standard deviation of 5%. It is noticeable that the analyte recovery rate is very low, from less than 1 % to 30 % for benzene.

Since a toner consists mainly of carbon and behaves like an adsorbent, it is probably capable of strongly adsorbing VOCs, in particular the semivolatile substances from this material class. This has the consequence that this analysis method is not capable of accurately determining the original composition of the toner.

This behaviour improves, when the internal standards are considered in the evaluation. Figure 14 shows the analyte recovery rate with and without correction, whereby the first columns (grey) represent analyte recovery rates without correction by any of the two internal standards (d_6 benzene or d_9 styrene). The next two columns (white and chequered) show the analyte recovery rates in the form of calculated analyte recovery rates using the added internal standards. When doing this, the components between benzene and stryrene are related to d_6 benzene or d_9 styrene, thus 100 % is obtained for both benzene and styrene. The white columns represent the evaluation using d_6 benzene from benzene to n-propylbenzene and the chequered columns represent the evaluation from ethylbenzene to styrene using d_9 styrene as an internal standard. However, depending on which of the internal standards is used to perform the calibration, the values show considerable changes both positive or negative for the intermediate compounds that have not been determined using the deuterated standards and this results in considerable deviations in the sums of the VOC. In order to obtain more reliable values within the range between styrene and benzene, the range of deuterated standards used should be considerably increased.

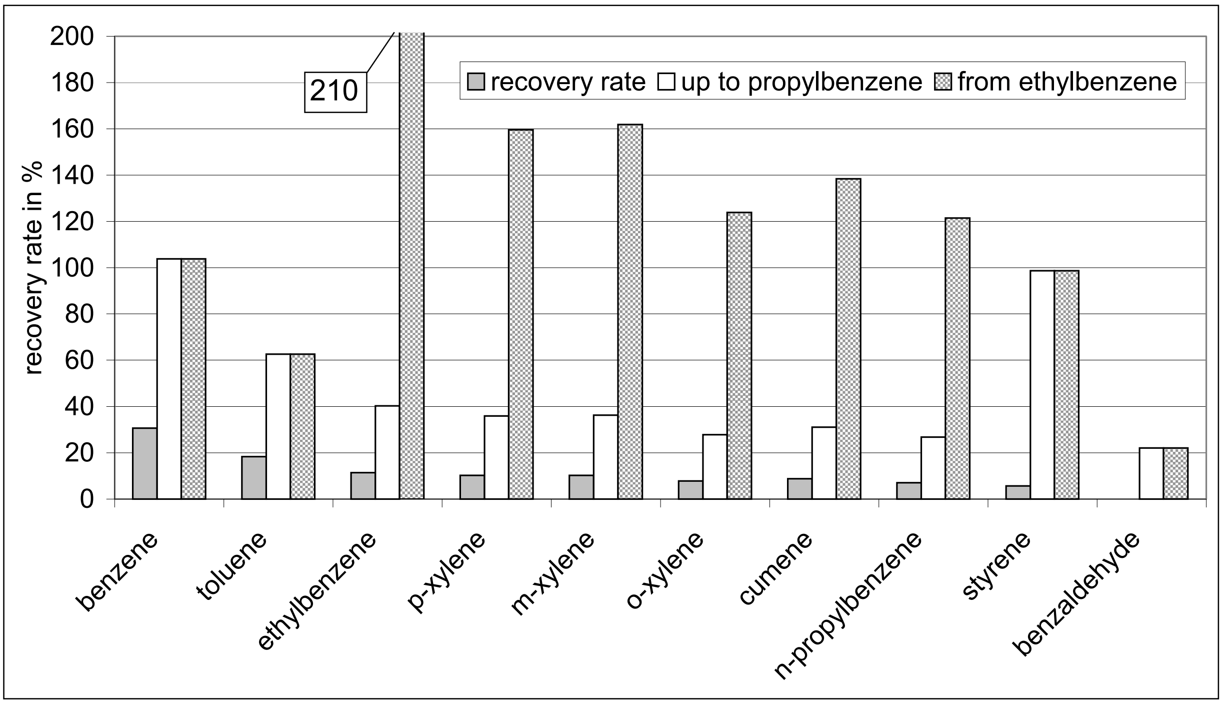


Figure 14: Determination of analyte recovery rates for standard compounds added in a solution to a toner - compared to an empty headspace glass. Analyte recovery rates of standard substances with a toner: evaluated without an internal standard, up to n-propylbenzene using d_6 benzene and from ethylbenzene using d_9 styrene (see details in text).

4 Procedure

4.1 Devices and consumable materials

4.1.1 Description of the hardcopy devices tested

Altogether ten different laser printers and copiers of seven manufacturers were tested. The copiers tested were operated via an option as printers during the tests on gounds of measurement technics. All devices were modern devices which are currently used in offices. The individual devices are described briefly in the following:

Device 0

This was a laser printer from manufacturer A available in BAM and used in the preliminary tests.

Devices 1, 8 and 9

Hardcopy devices one, eight and nine were brand-new laser printers (desktop devices) of the same type from manufacturer A. Device 1 was selected for the co-operative test. Since device one had to be scratched due to damage in the co-operative test, device eight was used in the subsequent investigations. After returning devices one and eight to be tested in the manufacturer’s laboratory, further comparative tests were performed on device nine. The 250-sheet paper tray of the devices was replaced with a 500-sheet paper tray to enable printing 500 sheets in one go.

Device 2

Hardcopy device two was a brand-new copier (small freestanding device) from manufacturer B. The copier was operated using the printer option during the tests because of measurement technical aspects. Since it was the aim to print 500 sheets in one go, a mechanical appliance was built which made it possible to empty the output tray when filled with about 250 sheets. This was performed without opening the emission test chamber.

Device 3

Hardcopy device three was a brand-new laser printer (desktop device) from manufacturer C. Printing 500 sheets was no problem.

Device 4

Hardcopy device four was a brand-new copier (small freestanding device) from manufacturer D. This copier too had to be operated via the printing option during the tests on grounds of measurement technics. Comparative tests, whether emission behaviour changes when the device is operated as a copier have not been performed. Since it was the aim to print 500 sheets in one go, a mechanical appliance was built, which made it possible, to empty the output tray when filled with about 250 sheets. This was performed without opening the emission test chamber.

Device 5

Hardcopy device five was a brand-new copier (small freestanding device) from manufacturer E. This copier too had to be operated with the printer option during the tests on grounds of measurement technics. Printing 500 sheets was no problem.

Device 6

Hardcopy device six was a brand-new copier (large freestanding device) from manufacturer F. This copier too had to be operated with the printer option during the tests on grounds of measurement technics. Since it was capable of printing 2500 sheets in one go, a mechanical appliance was built, which made it possible, to empty the paper stacker after about the half of the printing time. This was performed without opening the emission test chamber.

Device 7

Hardcopy device seven was a used laser printer (desktop device) from manufacturer G. Printing speed of this device was in comparison to other laser printers tested comparatively low. Refitting the device to handle 500 sheets was not possible.

4.1.2 Description of consumable materials

4.1.2.1 Toner

While developing the test procedures, original toners belonging to the actual devices were used in the emission tests.

In addition to the emission tests 32 different toners from twelve suppliers were tested using the static headspace method. For a simultaneous co-operative test six different samples were selected from this pool of 32 different toners. The original idea was to reduce device emissions markedly by restricting the VOC content of the toners.

4.1.2.2 Paper

Table 11 gives an overview of the papers used for printing. Both new and recycled papers were used. The papers used met the requirements of DIN 19309 (Papier für Kopierzwecke, Paper for copying) [8], which was still valid at the time of the tests. From January 2003 this standard was replaced with DIN EN 12281 (Druck- und Büropapier - Anforderungen an Kopierpapier für Vervielfältigungen mit Trockentoner“ - Printing and office paper - Requirements on copying paper for duplication with dry toner; 2002) [10].

The exact type of paper and manufacturer data are coded. For all emission measurements on recycled paper (type ’0’), the paper was dried in a drying furnace in order to prevent a water vapour condensation during printing in the A and B type 1m³ test chambers after the preliminary tests (see 5.2) showed a water content of 3.6 % to 4.2 %.

Table 11: Overview of paper types used for printing

Paper type	Manu-facturer	Paper description	Format per DIN	Mass per area [g m^{-2}]	Water content* [%]
0	R	Copying paper 60 white	A4	80	5.5
1	S	New, white	A4	80	4.2
2	T	New, white	A4	80	4.8
3	X	New, white	A4	80	4.2
4	Y	New, white	A4	80	4.2

---

[*] Determined in BAM per DIN EN 20287 „Measurement of moisture content“ [11]

4.2 Investigations performed

VOC, dust and ozone emissions were measured on all devices, certain devices were tested several times, sometimes under different conditions. The original objective was to have several devices tested by various co-operative test participants and perform reference tests in the BAM before, between and after each co-operative test measurement.

4.2.1 Measurement procedure

4.2.1.1 Chamber characterisation and blank valuation before tests

- Chamber blank valuation for VOC, dust and ozone
- Adjustment and determination of air exchange rate of the chamber as per DIN V ENV 717-1 (1998) in an empty state
- Determination of ozone half-life as a substantial quality criterion for an empty chamber

4.2.1.2 Printing tests and calibration of hardcopy devices to be tested

- General functionality check of hardcopy devices after delivery
- Trial printing (test pages with 5 % black coverage, black per DIN 33870 [9] (see also Figure and Figure in Appendix), to avoid disruptions of the printing process during measurements in the test chamber
- Determining the maximum printing time
- Checking proper paper stacking and, if necessary, installing an additional receptacle container of inert material – capacity of paper cassette and paper output tray had to be taken into account
- Calibration of hardcopy devices to be tested by means of printing templates per DIN 33870 [9] (http://www.ps.bam.de/DG02/DG02.HTM , „X10GS3PN.PDF“)

4.2.1.3 Cold and standby phase

Cold and standby phases were taken over two hours in each case. The cold phase was defined as „switched-on power switch, but disconnected power plug from current supply”. The aim of this arrangement was to allow starting the hardcopy device to be tested in the subsequent standby phase from the outside by simply inserting the plug into the socket without opening the chamber.

At the beginning of the standby phase the hardcopy device to be tested was connected to the current supply by putting the power plug into the socket. A two-hour standby phase was possible without any problem in all devices tested.

First, during the cold and standby phase, ozone, dust and VOC were measured. When it was shown that no measurable dust and ozone emissions arose during any of these phases, it was left out of ozone and dust measurements later during these phases. Climate recording began with the start of the cold phase and was continuously performed to the end of the follow-up phase. Air exchange rate was adjusted to $n = 1\ h^{-1}$ in all chambers during the cold and standby phase.

The paper to be printed was not placed in the device during the cold and standby phase of these tests as it was unknown whether the paper had its own emission or not.

4.2.1.4 Opening the chamber and placing paper in the device

The chamber was opened after the end of the standby phase, the paper to be printed inserted into the device and the chamber closed again. In the 20m³ chamber, the air exchange rate remained adjusted to $n = 1\ h^{-1}$. However, the air exchange rate in the 1m³ chambers was adjusted to $n = 4$ to $4.7\ h^{-1}$ at dry air (< 10 % R. H) in order to keep relative humidity, which rose during printing due to water release from the paper, below critical values (see also 5.2 and 6.1).

Afterwards a 30-minute chamber equilibration was performed, so that a defined initial value of relative humidity was achieved at the beginning of the subsequent printing phase. This amounted to 50 % R. H. in the 20m³ chamber and to 10% to 20% R. H. in the type A and B 1m³ chambers.

4.2.1.5 Printing and follow-up phase

The printing phase lasted up to 36 minutes when the device tested printed 500[*] sheets of paper. The follow-up phase was consecutive and under identical test conditions and served to collect all emitted substances if possible, after the actual printing job had finished.

The follow-up phase took thirty minutes on the grounds of measurement technics. Towards the end of the tests it was increased to four air exchange rates in order to ensure a complete collection of the emitted substances. The follow-up phase then took about four hours for the 20m³ chamber and about one hour for the 1m³ chambers.

Ozone determination started immediately at the beginning of the printing job and was continued to the end of the follow-up phase. If a suitable concentration range was selected, this could be recorded permanently with electronic dataloggers. Ozone half-life needed for the calculation of ozone emission rate was determined afterwards from the decay curve in the follow-up phase with sufficiently large concentrations. At this time the test conditions of the printing phase still approximately existed. If the ozone concentration to be determined during the printing job was too small, determination of ozone half-life was performed after the test by adding 0.1 ppm to 0.2 ppm ozone with the help of an ozone generator in the still unopened chamber and recording this ’artificially created’ ozone decay curve.

Dust measurement started likewise immediately at the beginning of the printing job and was continued to the end of the follow-up phase. Air taken during this time from the test chamber was sucked by a pump through a glass-fibre filter. The volume of air sucked through the filter was determined. Differential weighing of the filter provided the absolute dust mass in µg. From both values dust concentration in the test chamber was calculated (in $\mu g\ m^{-3}$) and from this the dust emission rate (in $\mu g\ h^{-1}$). The specific emission rate was corrected for climate (see Paragraph 3.3.2).

---

[*] 500 sheets: maximum number of sheets to be printed by desktop devices in one step without opening the chamber, to ensure as long a printing time as possible to achieve an equilibrium.

VOC sampling was subdivided into three or four periods during the printing phase. For each subphase, VOC determination was accomplished over the entire subphase. The original aim of this subdivision was to compare actual measured concentrations with values predicted by theory, cf. 2.4 „Theoretical considerations“.

A supplementary VOC sampling was performed over the entire follow-up phase.

A further VOC sampling extended from the beginning of the printing phase to the end of the follow-up phase, in order to enable a comparison of the VOC emission rate determined in this way with VOC emission rates obtained through partial sampling.

4.2.1.6 Final work

- Device and paper removal
- Chamber clean-up
- Preparation for the next test
- Evaluation of test results

5 Results of emission tests

5.1 General considerations

In order to enable reliable statements on the emission behaviour of the devices tested, different test conditions were selected. These included for example the use of different emission test chambers, different types of printing paper and printing with different black coverage. Repetition measurements under constant test conditions likewise took place.

A large number of test data were collected during the project. Table 8 in the appendix shows the exact measured values. In order to systematise and interpret the obtained data, the results of the emission tests are arranged and evaluated in the following groups based on the devices.

5.2 Preliminary tests

The preliminary tests were accomplished on device 0 in the type B 1m³ chamber and they provided the foundation for all further tests, cf. also Chapter 6. „Investigations to improve the testing methods“. When using recycled paper (which was an initial default of the project commissioning agency[§]), relative air humidity rose rapidly during the printing process in the type B 1m³ chamber. In ceratin cases even condensation of water vapour occurred in the test chamber. The recycled paper was therefore dried to a maximum water content of between 3.6 % and 4.2 % for all further tests (cf. also 0 and 6.1) and the air exchange rate was increased to 4 or 5 h^{-1}. Similar problems were not experienced with the 20m³ chamber.

[§] In addition, recycled paper is used for tests as per current selection criteria

5.3 Main tests

5.3.1 Device 1

Device 1 was tested in both repetition measurements under standard conditions, i.e. with 5% black coverage using recycled paper (P 0) and with the different types of new paper P 1, P 2, P 3 and P 4. In addition 500 empty sheets of paper 0 were printed, which corresponds to 0 % black coverage.

Figure 15 and Figure 16 illustrate the results of the gravimetric dust and TVOC measurements. None of the preformed tests yielded any measurable ozone emission during printing.

Comparing the results of the tests on recycling paper of 26 and 27 February with those of 17 April, it becomes clear that SER_D shown in Figure 15 decreased by about 50 % in relation to the first measurement. It was however expected that printing empty sheets on 27 February would yield lower SER_D. The result obtained on 27 February was confirmed on 17 April using 5 % black coverage. SER_D values determined on different types of new paper P 1, P 2, P 3 and P 4 are, except for Paper 1, within the range of 0.4 to 0.6 mg per unit and hour. They are somewhat lower than the values measured on recycled paper, however they are relatively constant in the same order of magnitude.

The results suggest that the tested printer had first to achieve a certain "operational status" in order to emit less dust than in the first test.

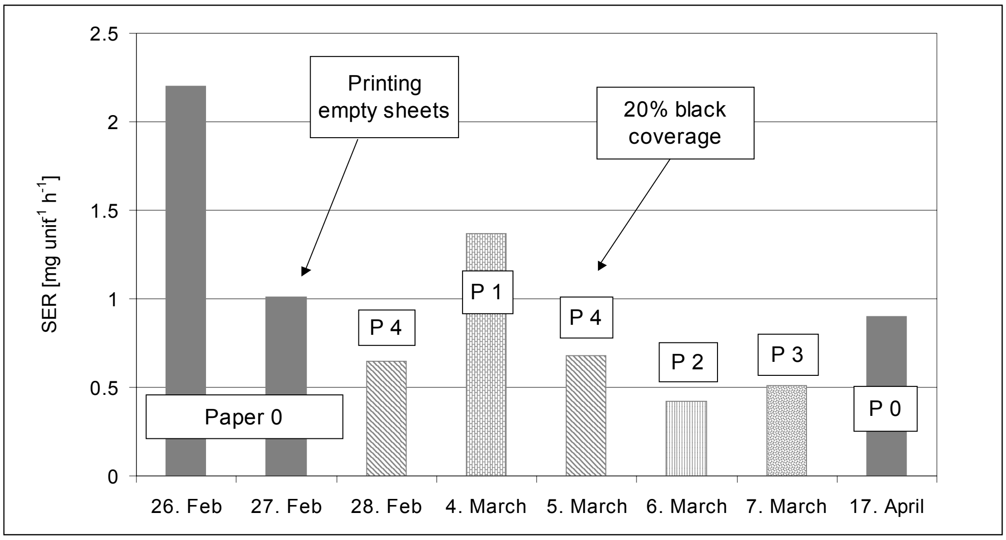


Figure 15: SER_P determined by gravimetric test: device 1, 8 tests, 5 sorts of paper, type A 1m³ chamber

Figure 16 shows the TVOC emission rates for all eight tests. By far the greatest TVOC concentration among the tests on device 1 was obtained for paper P4 with 20% black coverage. The value 10.4 mg unit^{-1} h^{-1} amounts to nearly a fivefold increase from the 2.2 mg unit^{-1} h^{-1} determined when using the 5% standard black coverage. Other TVOC values determined within a relatively short period for P1, P2 and P3 are nearly the same. It should be noted that the TVOC values of device 1 with recycled paper P0 exhibit a decaying tendency in the period from 26 February to 17 April.

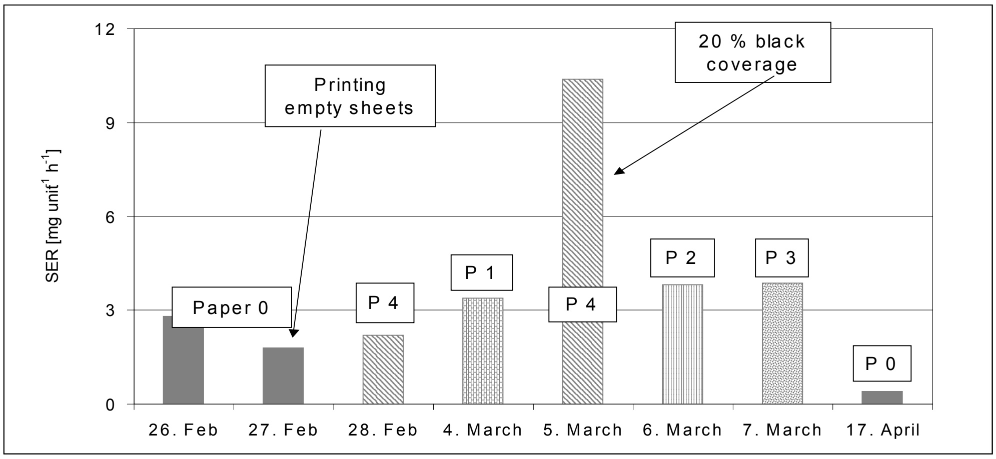


Figure 16: SER$_{TVOC}$ for device 1: 8 tests, 5 sorts of paper, type A 1m³ chamber

Xylenes, as well as hexanal, benzaldehyde, phenol and styrene were the main emissions among the VOC values in the printing phase (D 3, end of printing phase) (Table 12, day of measurement: 26 February), in addition to a number of other compounds exhibiting significant values. Phenol represented the main emission in the cold phase and benzaldehyde in the standby phase.

Table 12: VOC emission rates [µg unit^{-1} h^{-1}] for device 1, first test

Substance	**Cold**		**Standby**		**Printing and follow-up phase**				
	C 1	**C 2**	**St 1**	**St 2**	**Pr 1***	**Pr 2***	**Pr 3***	**F***	**Pr 3**
Benzene	---	**ND**	---	**ND**	**ND**	**ND**	**ND**	ND	**ND**
Toluene	---	**ND**	---	**ND**	40	24	64	12	**92**
Hexanal	---	**ND**	---	**ND**	60	168	228	72	**326**
Ethylbenzene	---	**4**	---	**4**	40	104	124	44	**177**
m,p-Xylene	---	**5**	---	**4**	56	148	164	48	**235**
Styrene	---	**7**	---	**9**	56	140	180	64	**258**

Substance	**Cold**		**Standby**		**Printing and follow-up phase**				
	C 1	**C 2**	**St 1**	**St 2**	**Pr 1***	**Pr 2***	**Pr 3***	**F***	**Pr 3**
Heptanal	---	**1**	---	**1**	12	36	44	16	**63**
o-Xylene	---	**3**	---	**3**	48	128	164	48	**235**
Benzaldehyde	---	**5**	---	**58**	88	196	248	64	**355**
Phenol	---	**16**	---	**25**	88	188	180	108	**258**
Ethylhexanol	---	**ND**	---	**3**	16	24	24	12	**34**
Acetophenone	---	**2**	---	**2**	52	116	136	36	**195**
Nonanal	---	**2**	---	**2**	24	4	72	24	**103**
BHT	---	**1**	---	**3**	4	4	ND	4	**0**
Pentadecane	---	**ND**	---	**1**	4	116	140	48	**200**
Hexadecane	---	**1**	---	**2**	64	176	208	8	**298**
TVOC	---	**47**	---	**117**	652	1572	1976	608	**2828**

Columns marked with * contain apparent emission rates, as the short printing time did not allow for an equilibrium to develop and/or the follow-up phase also failed to establish an equilibrium, thus concentrations were still decreasing.
ND: Non-detectable

Figure 17 illustrates the chromatogram of a GC/MS run of 26 February. The analysed sample was taken during the printing phase. This test was performed on recycled paper. As a comparison, Figure 18 shows the chromatogram of a GC/MS run of 4 March. The analysed sample was likewise taken during the printing phase. However this test was performed on new paper 1 (P 1).

A comparison of the two chromatograms clearly shows a higher fraction of SVOC emissions when using recycled paper, if one regards the "hill" in the retention time interval between minutes 28 and 34 in Figure 17. It has to be noted that the SVOC range begins at 28.4 minutes. This corresponds to the retention time of the n-hexadecane. The connection between paper type and SVOC emissions was confirmed by direct thermodesorption of the individual types of paper. These investigations are described in detail in Section 6.2.

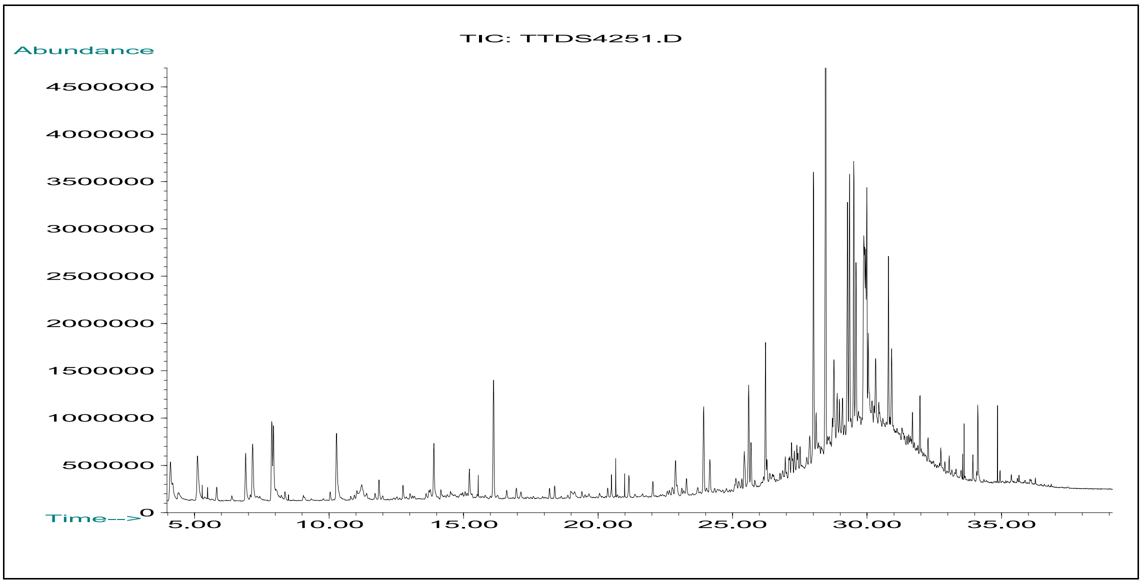


Figure 17: Chromatogram of 26. February from the printing phase: recycled paper (P 0), device 1, type A 1m³ chamber

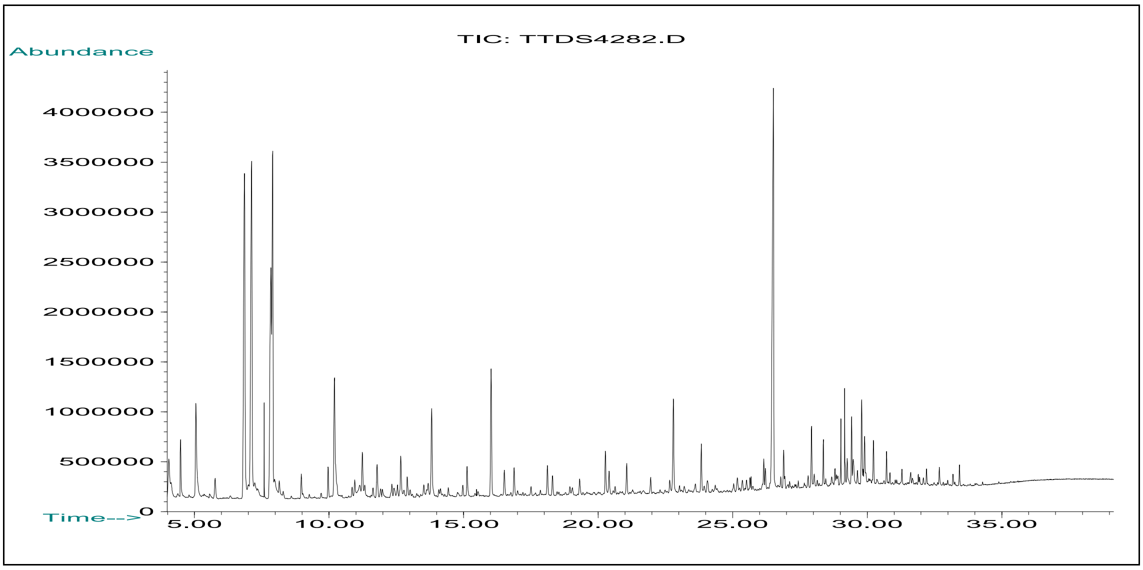


Figure 18: Chromatogram of 4. March from the printing phase: new paper (P 1), device 1, type A 1m³ chamber

5.3.2 Device 2

One test was carried out on device 2 and the results are shown in Figure 19. Dust, TVOC and ozone emission rates obtained were remarkably low in comparison to other devices, while ozone emission was just detectable for this device.

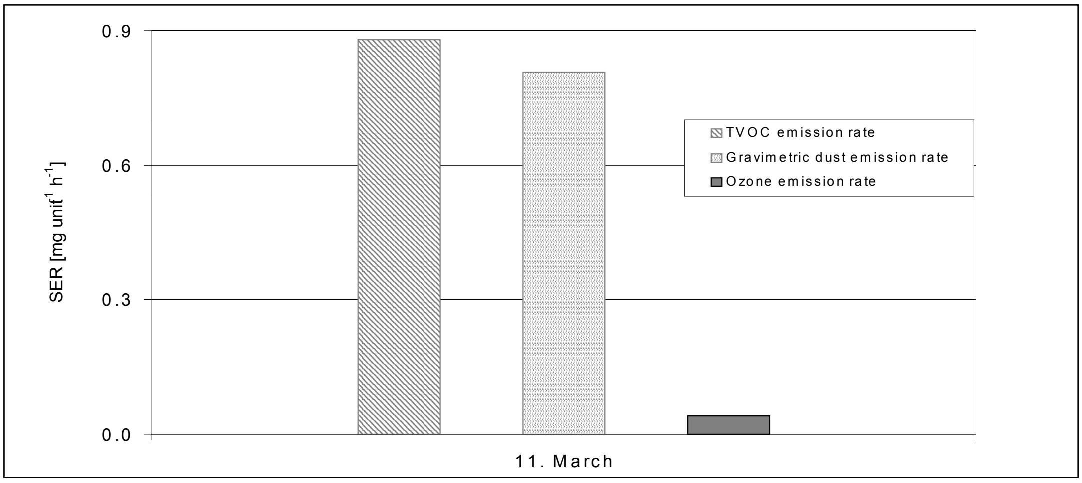


Figure 19: Emission rate overview for device 2: one test, paper 0, type A 1m³ chamber

Hexanal and hexadecane were the main emittents in the printing phase among VOCs in addition to a number of further VOCs with emission rates of less than 100 µg h^{-1}. Toluene and phenol were the main emittents in the cold and standby phase.

Table 13: VOC emission rates [µg unit^{-1} h^{-1}] for device 2

Substance	Cold		Standby		Printing and follow-up phase					
	C 1	C 2	St 1	St 2	Pr 1*	Pr 2*	Pr 3*	Pr 4*	F*	Pr 4
Benzene	---	**ND**	---	**ND**	ND	ND	ND	ND	ND	**ND**
Toluene	---	**11**	---	**12**	120	140	120	76	32	**88**
Hexanal	---	**ND**	---	**ND**	236	100	144	168	60	**195**
Ethylbenzene	---	**2**	---	**8**	12	16	20	20	16	**23**
m,p-Xylene	---	**1**	---	**3**	4	8	8	8	4	**9**
Styrene	---	**1**	---	**2**	16	28	32	40	16	**46**
Heptanal	---	**1**	---	**1**	8	16	20	24	52	**28**
o-Xylene	---	**5**	---	**1**	ND	4	4	4	4	**5**
Benzaldehyde	---	**3**	---	**6**	40	44	60	44	ND	**51**
Phenol	---	**8**	---	**18**	52	60	76	72	52	**84**
Ethylhexanol	---	**5**	---	**7**	16	20	20	24	12	**28**
Acetophenone	---	**3**	---	**3**	20	24	28	20	36	**23**
Nonanal	---	**4**	---	**6**	36	60	56	68	36	**79**
BHT	---	**ND**	---	**3**	ND	12	ND	12	12	**14**
Pentadecane	---	**1**	---	**1**	16	48	60	68	28	**79**
Hexadecane	---	**1**	---	**2**	28	64	84	92	40	**107**
TVOC	---	**46**	---	**73**	604	644	732	740	400	**859**

Columns marked with * contain apparent emission rates, as the short printing time did not allow for an equilibrium to develop and/or the follow-up phase also failed to establish an equilibrium, thus concentrations were still decreasing.
ND: Non-detectable

5.3.3 Device 3

Device 3 was also tested in several repetition tests. The tests were first performed on recycled paper (P 0) over a longer period. In December, for the purpose of comparison, new paper 1 was tested: 250 sheets (5 December, first value) and 500 sheets (5 December, second value) were printed. Furthermore, on 12 December 250 sheets of new paper 1 were tested in a comparison test in the 20m³ chamber.

Figure 20 shows the results of the gravimetric dust measurements. A comparison of the results of the tests of 12 March to 20 June on recycled paper in the 1m³ chambers A and B indicates that the SER_D values exhibit only small differences and are very reproducible. In contrast, SER_D determined on the new paper 1 on 5 December are markedly smaller. A certain dependence of the dust emission on the type of paper used for printing seems to exist.

Gravimetric dust regulation in the 20m³ chamber shows a completely different picture. SER_D of 5.0 obtained in the test on new paper 1 on 5 December provided a value of 50 fold in comparison with the type B 1m³ chamber under otherwise constant test conditions. An increased dust blank value in the 20m³ chamber was excluded by repetition measurements.

The sampling seems to be the reason for the high SER_D. Sampling took place in the 20m³ chamber in accordance with the conditions of the ECMA standards [18] near the device to be tested within the test chamber. This kind of sampling seems to yield inhomogeneities in the dust distribution during the printing process, so that an absolute dust amount higher by about a factor three was obtained than in the type B 1m³ chamber from which then a higher SER_D can be calculated. In contrast, dust sampling took place centrically at the wall in the type A and B 1m³ chambers by screwing the filter container onto a threaded connection point, which is more likely to enable a homogeneous sampling.

SER_D values, which were very high in comparison with the type A and B 1m³ chambers, were experienced in the 20m³ chamber with all devices tested in a comparative chamber test.

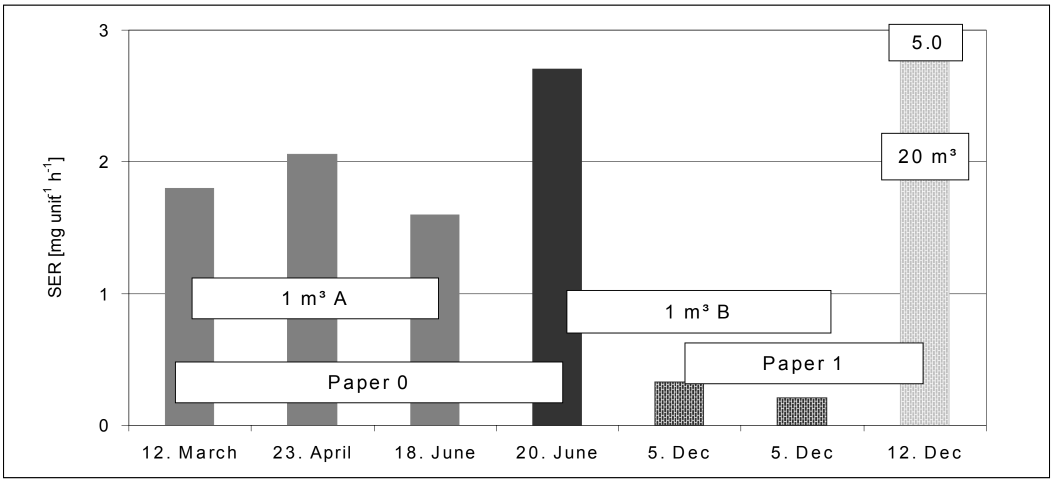


Figure 20: SER$_D$ determined in device 3 using gravimetric tests: 7 tests, 2 sorts of paper, type A and B 1m³ chambers, 20m³ chamber

The TVOC values, except the last two measurements, tend to show constant emissions (Figure 21), even over the long period from 12 March to 24 September. The tests on 5 December indicate larger differences. In addition, a different emission pattern was found in contrast to the previously performed tests. Thus ethylene glycol and propylene glycol appeared as new pollutants for example and exhibited strongly varying emissions. Since the device had a defect before the tests, which was repaired by the customer service on 5 December, it is probable that emission behaviour changed due to this interference.

The VOC emission spectrum determined at the beginning of the investigations on device 3 can be seen in Table 14. It is noticeable that the main emittent was a non-identifiable VOC and a group of compounds (denoted by ’alkane hill’ in Table 14). It was not possible to make an exact identification and quantification of this group. These compounds were therefore quantified by the response factor of toluene. Phenol and alkanes (’alkane hill’) were the main emittents in the cold and standby phase, however the non-identifiable compound from the printing process was not found here. This indicates an emission from the toner during the printing process, as the non-identified compound was also found in the toner investigations (see Section 6.3).

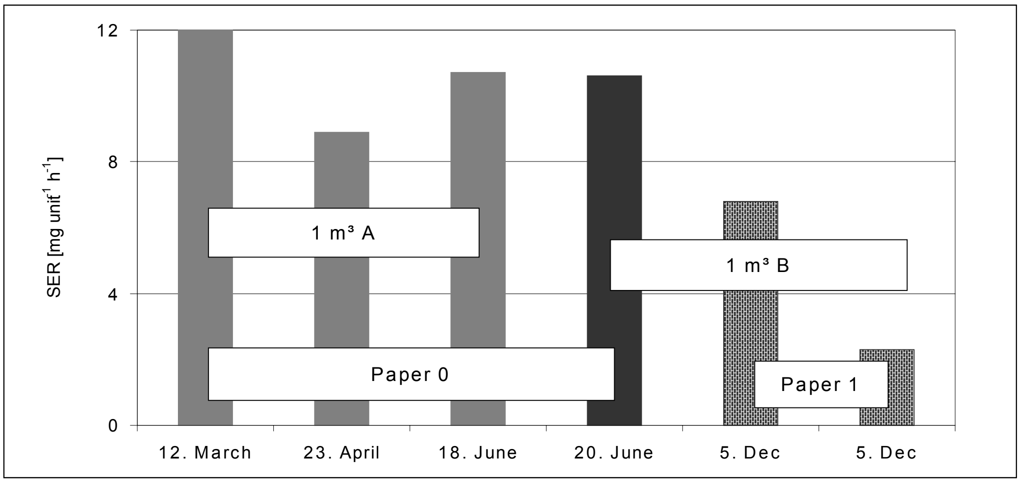


Figure 21: SER$_{TVOC}$ for device 3: 6 tests, 2 sorts of paper, type A and B 1m³ chambers, 20m³ chamber

Table 14: VOC emission rates [µg unit^{-1} h^{-1}] for device 3, first test

Substance	Cold		Standby		Printing and follow-up phase				
	C 1	**C 2**	**Sb 1**	**Sb 2**	**Pr 1***	**Pr 2***	**Pr 3***	**F***	**Pr 3**
Benzene	---	**ND**	---	**ND**	ND	ND	ND	ND	**ND**
Toluene	---	**15**	---	**17**	24	28	40	20	**58**
Hexanal	---	**1**	---	**3**	76	212	320	128	**461**
Ethylbenzene	---	**2**	---	**3**	48	112	156	68	**225**
m,p-Xylene	---	**2**	---	**2**	16	28	40	16	**58**
Styrene	---	**3**	---	**10**	24	48	68	44	**98**
Heptanal	---	**1**	---	**2**	20	68	96	44	**138**
o-Xylene	---	**1**	---	**1**	20	44	64	28	**92**
Benzaldehyde	---	**6**	---	**7**	116	264	380	132	**548**
Phenol	---	**23**	---	**43**	180	292	392	204	**565**
Alkane hill	---	**41**	---	**37**	1180	3432	4572	1320	**6588**
Ethylhexanol	---	**3**	---	**5**	8	16	20	12	**29**
VOC, unidentified	---	**ND**	---	**ND**	388	988	1216	412	**1752**
Acetophenone	---	**2**	---	**2**	28	52	76	24	**110**
Nonanal	---	**4**	---	**6**	104	344	440	224	**634**
BHT	---	**ND**	---	**3**	116	168	204	156	**294**
Pentadecane	---	**1**	---	**1**	36	88	116	36	**167**
Hexadecane	---	**2**	---	**2**	52	116	152	52	**219**
TVOC	---	**107**	---	**144**	2436	6300	8352	2920	**12035**

Columns marked with * contain apparent emission rates, as the short printing time did not allow for an equilibrium to develop and/or the follow-up phase also failed to establish an equilibrium, thus concentrations were still decreasing.
ND: Non-detectable

The results of repeated ozone measurements, shown in Figure 22, display a noticeably good agreement over a long period of time, despite the problems discussed above. Some additional measurements were carried out for ozone in order to decide whether a number of printing processes possibly lead to an increase in ozone emission rate during a longer period. As can be seen, no increase was experienced. The ozone emission rates determined were easy to reproduce, although the ozone emission level was relatively high. Device 3, together with device 4, exhibits the highest ozone emission rate measured within this project.

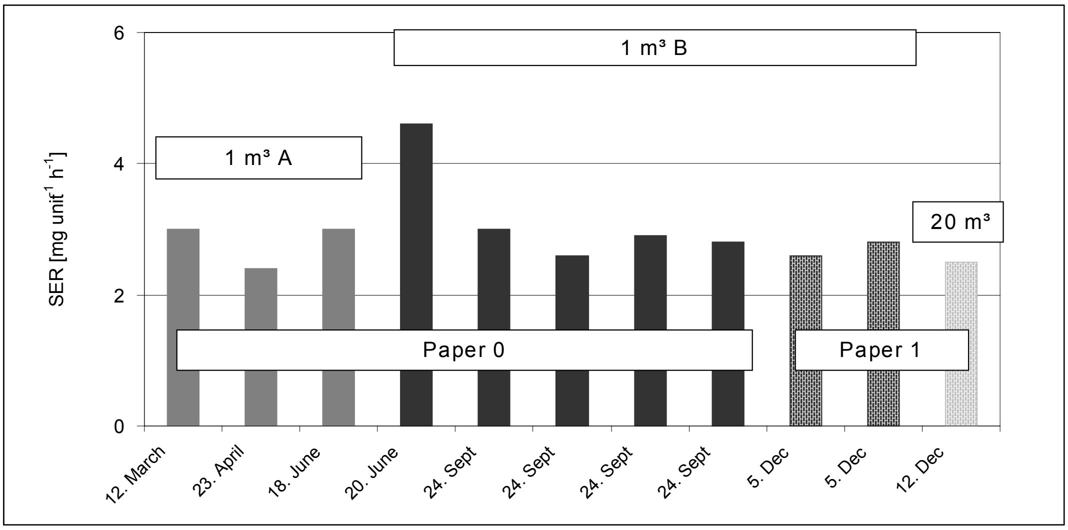


Figure 22: SER_{ozone} for device 3: 11 tests, 2 sorts of paper, type A and B 1m³ chambers, 20m³ chamber

5.3.4 Device 4

Comparative measurements among the available three test chambers were performed on device 4 using recycled paper (P 0).

A comparison of the test results on recycled paper in the period of 14 March to 3 July shows that SER_D illustrated in Figure 23 clearly decreases regardless of the 1 m³ chamber used. A qualitative correlation with the results of the TVOC measurements is given by Figure 24. The results suggest that the tested printer, similar to device 1, first had to achieve a certain "operational condition", in order to emit less dust than at the beginning.

The gravimetric dust determination in the 20m³ chamber shows a completely different picture. The test on new paper P 1 on 5 December resulted in 5.0 for SER_D, a drastically increased value in comparison with the type B 1m³ chamber, under otherwise constant test conditions. An increased dust blank value in the 20m³ chamber was excluded by repetition measurements. The explanation given in connection with device 3 may also apply to this behaviour.

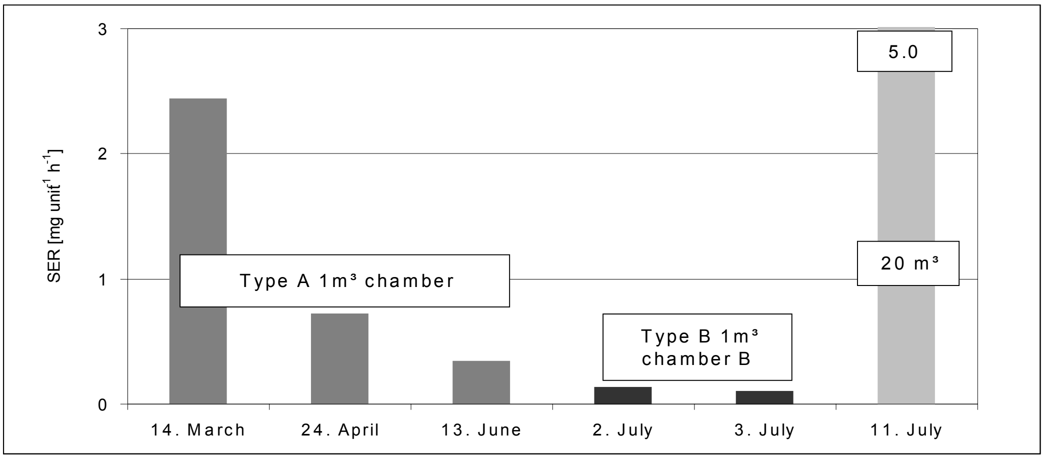


Figure 23: SER_D determined using gravimetric tests: device 4, 6 tests, paper 0

TVOC values (Figure 24) also show a decay as a function of time, while comparative chamber tests temporally closer to each other exhibited a relatively good agreement.

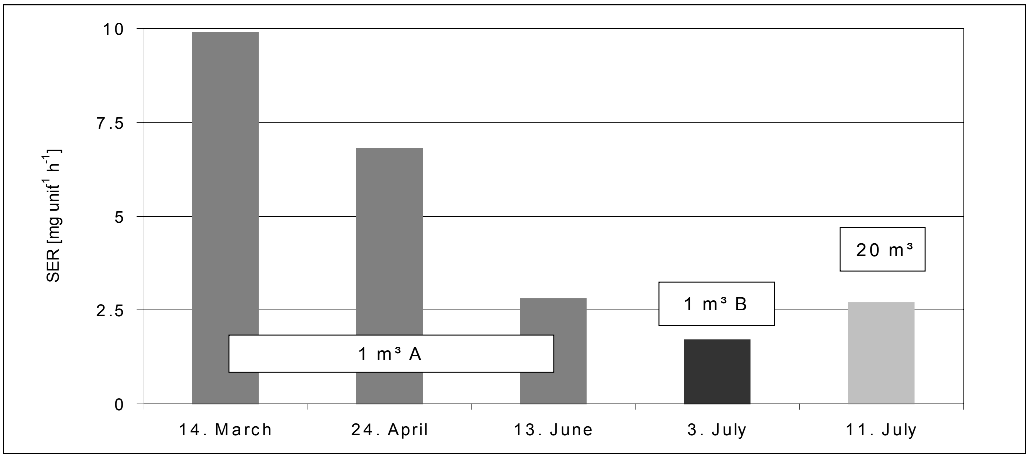


Figure 24: SER_{TVOC} for device 4: 5 tests, paper 0

The VOC emission spectrum determined at the beginning of the investigations on device 4 can be taken from Table 15. Toluene appeared here as a marked main component, which was also contained in the toner, but only in a comparatively small proportion, see also Section 6.3. Obviously there was another important source of toluene in this device. Other compounds, such as styrene, ethylbenzene, xylene and nonanal were also present in higher concentrations. Nonanal appeared as a reaction product of ozone with Tenax and possibly also as a reaction product of ozone with volatile organic compounds. The compounds mentioned were the main emitted substances in the cold and standby phase.

Table 15: VOC emission rates [µg unit^{-1} h^{-1}] for device 4, first test

Substance	**Cold**		**Standby**		**Printing and follow-up phase**					
	C 1	**C 2**	**St 1**	**St 2**	**Pr 1***	**Pr 2***	**Pr 3***	**Pr 4***	**F***	**Pr 4**
Benzene	---	ND	---	**ND**	ND	ND	ND	ND	ND	**ND**
Toluene	---	107	---	**833**	2764	4704	5436	5852	12	**6952**
Hexanal	---	1	---	**ND**	32	64	84	88	72	**105**
Ethylbenzene	---	15	---	**32**	180	324	416	444	44	**527**
m,p-Xylene	---	11	---	**23**	136	244	328	360	48	**428**
Styrene	---	58	---	**90**	360	480	640	712	64	**846**
Heptanal	---	1	---	**ND**	16	36	140	56	16	**67**
o-Xylene	---	5	---	**6**	60	104	140	148	48	**176**
Benzaldehyde	---	ND	---	**4**	32	144	164	120	64	**143**
Phenol	---	19	---	**13**	52	64	76	56	108	**67**
Ethylhexanol	---	27	---	**12**	56	52	60	60	12	**71**
Acetophenone	---	4	---	**2**	20	32	36	28	36	**33**
Nonanal	---	6	---	**3**	116	228	288	308	24	**366**
BHT	---	10	---	**9**	8	20	20	12	4	**14**
Pentadecane	---	1	---	**1**	8	20	24	24	48	**29**
Hexadecane	---	1	---	**1**	16	32	40	40	8	**48**
TVOC	---	266	---	**1029**	3856	6548	7892	8308	608	**9869**

Columns marked with * contain apparent emission rates, as the short printing time did not allow for an equilibrium to develop and/or the follow-up phase also failed to establish an equilibrium, thus concentrations were still decreasing.
ND: Non-detectable

This device too, similarly to device 3, produced greater ozone emissions, which were also at a comparatively constant level (Figure 25).

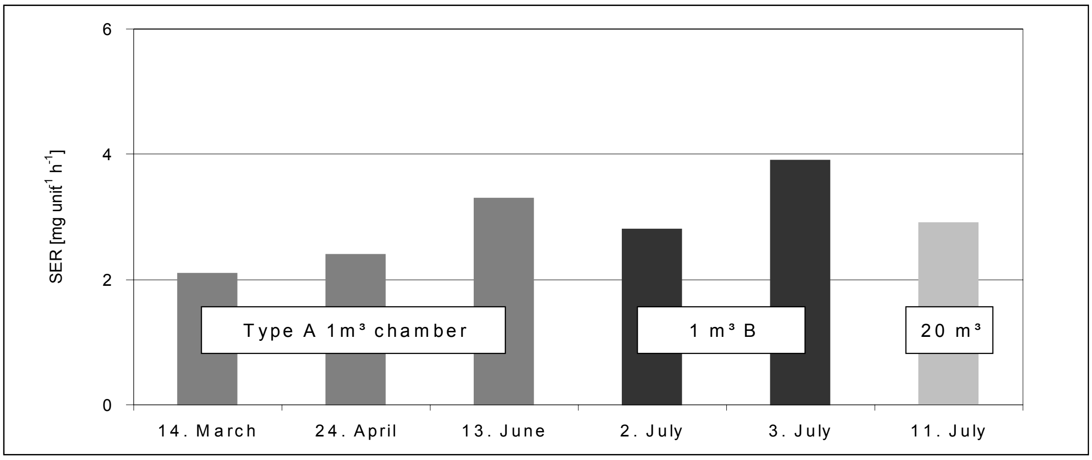


Figure 25: SER$_{ozone}$ for device 4: 6 tests, paper 0

5.3.5 Device 5

One test only was performed on device 5 in the 20m³ chamber because of its size. The results are displayed in Figure 26. Ozone emitted by this device was found to be just detectable.

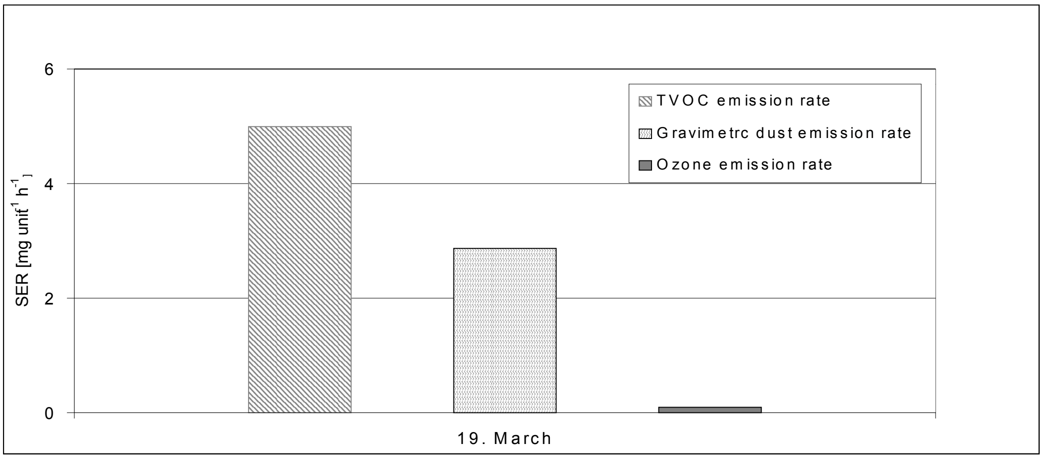


Figure 26: Emission rate overview for device 5: one test, paper 0, 20m³ chamber

As shown in Table 16, toluene was the main emission by this device, followed by benzaldehyde, benzylalcohol and acetophenone, and by high values of nonanal (cf. device 4). These compounds were also emitted in the cold and standby phase.

Table 16: VOC emission rates [µg unit^{-1} h^{-1}] for device 5

Substance	Cold		Standby		Printing and follow-up phase					
	C 1	**C 2**	**St 1**	**St 2**	**Pr 1***	**Pr 2***	**Pr 3***	**Pr 4***	**F***	**Pr 4**
Benzene	ND	**ND**	ND	**ND**	ND	ND	ND	ND	ND	**ND**
Toluene	600	**380**	280	**220**	200	660	700	560	160	**1955**
Hexanal	ND	**ND**	ND	**ND**	ND	ND	ND	ND	ND	**ND**
Ethylbenzene	20	**ND**	ND	**ND**	ND	ND	ND	ND	ND	**ND**
m,p-Xylene	20	**ND**	ND	**ND**	ND	ND	ND	ND	ND	**ND**
Styrene	ND	**20**	20	**20**	ND	ND	20	40	40	**140**
Heptanal	140	**ND**	20	**ND**	ND	ND	ND	40	20	**140**
o-Xylene	ND	**ND**	ND	**ND**	ND	ND	ND	ND	ND	**ND**
Benzaldehyde	100	**60**	60	**60**	160	160	80	200	60	**698**
Phenol	40	**40**	40	**60**	100	100	80	80	60	**279**
Benzylalcohol	380	**420**	240	**200**	60	180	180	180	ND	**628**
Ethylhexanol	20	**20**	20	**20**	ND	ND	ND	40	20	**140**
Acetophenone	20	**20**	40	**40**	20	80	40	200	40	**698**
Nonanal	60	**60**	40	**40**	20	80	120	120	60	**419**
TVOC	1400	**1020**	760	**660**	560	1260	1220	1460	460	**5097**

Columns marked with * contain apparent emission rates, as the short printing time did not allow for an equilibrium to develop and/or the follow-up phase also failed to establish an equilibrium, thus concentrations were still decreasing.
ND: Non-detectable

5.3.6 Device 6

Due to its size, device 6 could only be tested in the 20m³ chamber. Recycled paper was used in the tests.

The results of the gravimetric dust measurements, illustrated in Figure 27, show an increasing tendency in the dust emission rate. A measurable ozone emission during printing was not observed.

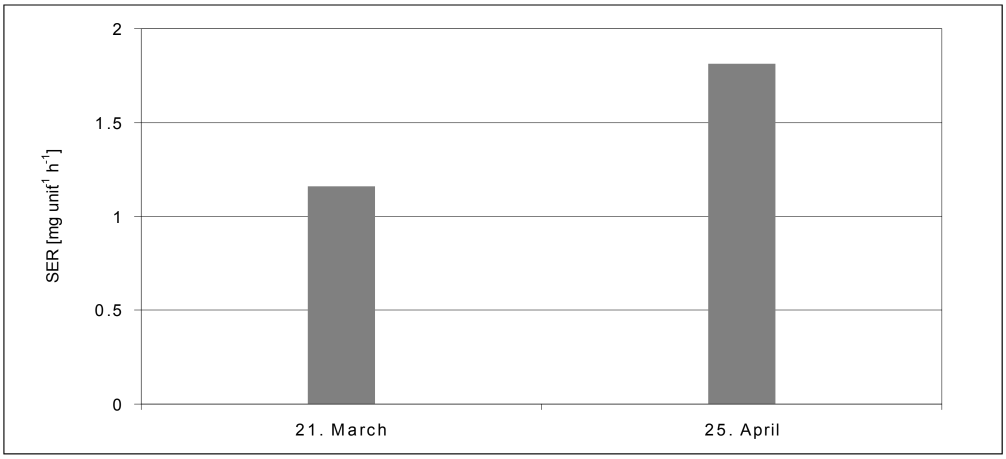


Figure 27: SER_D determined using gravimetric tests: device 6, 2 tests, paper 0, 20m³ chamber

The main emitted compound was propylene glycol, both in the printing phase and in the cold and standby phases, exhibiting remarkably high emission rates (Table 17). Further substantial compounds were benzaldehyde, acetophenone, nonanal and phenol, both in the printing and in the cold and standby phase.

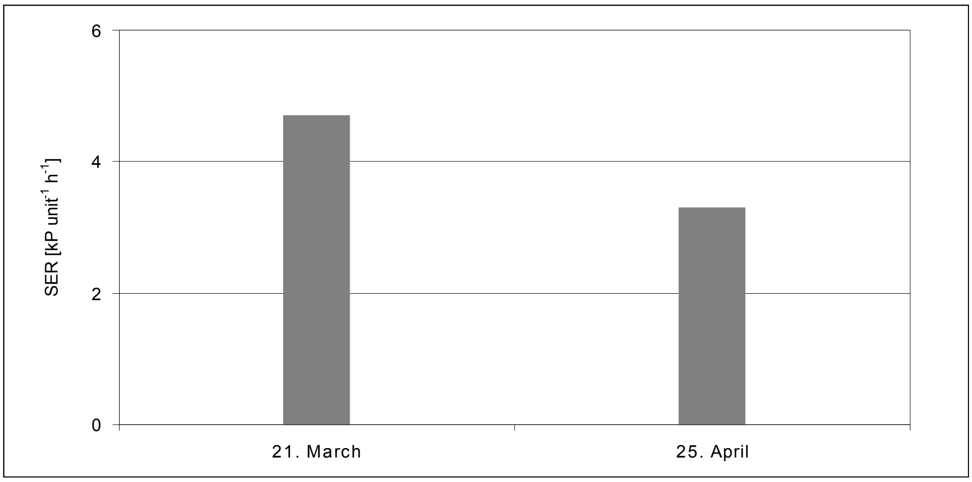


Figure 28: SER_{TVOC} for device 6: two tests, paper 0, 20m³ chamber

Table 17: VOC emission rates [µg unit^{-1} h^{-1}] for device 6, first test

Substance	**Cold**		**Standby**		**Printing and follow-up phase**					
	C 1	**C 2**	**St 1**	**St 2**	**Pr 1***	**Pr 2***	**Pr 3***	**Pr 4***	**F***	**Pr 4**
Benzene	ND	**ND**	ND	**ND**	ND	ND	ND	ND	ND	**ND**
Toluene	ND	**ND**	ND	**ND**	ND	ND	ND	ND	ND	**ND**
Hexanal	20	**ND**	ND	**ND**	ND	ND	ND	ND	60	**ND**
Ethylbenzene	20	**20**	20	**ND**	20	80	60	40	0	**113**
m,p-Xylene	20	**20**	60	**40**	80	60	60	40	40	**113**
Styrene	20	**20**	40	**60**	60	60	40	40	40	**113**
Propylene glycol	580	**520**	1360	**780**	640	940	760	660	1000	**1868**
Heptanal	20	**20**	40	**20**	ND	ND	ND	40	40	**113**
o-Xylene	ND	ND	20	**ND**	ND	20	ND	ND	20	ND
Benzaldehyde	40	**40**	120	**80**	300	220	200	160	80	**453**
Phenol	40	**60**	100	**80**	80	140	100	120	120	**340**
Ethylhexanol	40	**20**	60	**40**	40	60	40	40	40	**113**
Acetophenone	60	**40**	220	**220**	220	260	220	240	180	**679**
Nonanal	120	**100**	220	**160**	120	200	160	180	160	**509**
TVOC	980	**860**	2260	**1480**	1560	2040	1640	1560	1780	**4414**

Columns marked with * contain apparent emission rates, as the short printing time did not allow for an equilibrium to develop and/or the follow-up phase also failed to establish an equilibrium, thus concentrations were still decreasing.
ND: Non-detectable

5.3.7 Device 7

Equipment 7 was added to the measurement program at a later stage and it was tested in the type A 1m³ chamber under identical test conditions using recycled paper in repetition measurements on two consecutive days.

The results of the gravimetric dust determination, illustrated in Figure 29, are comparable with those of the other devices tested. The difference between the two determined values is due to the unreproducible emission behaviour of the equipment.

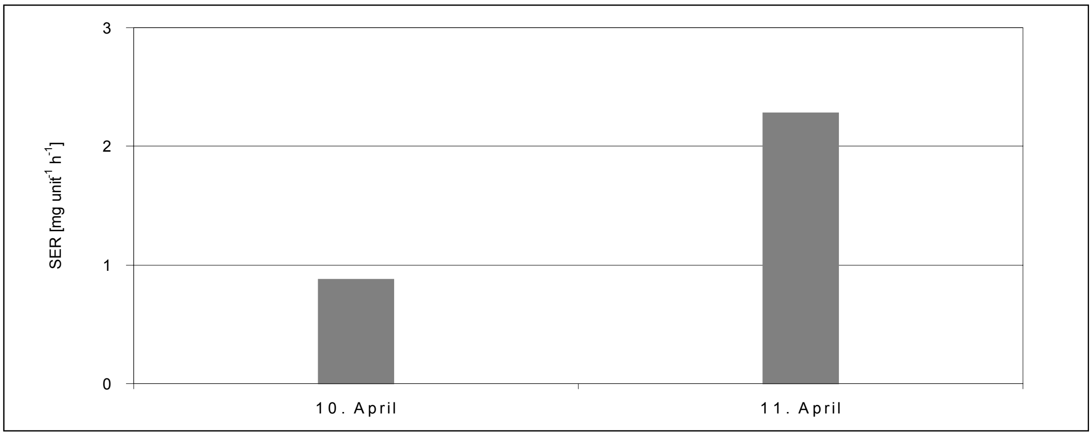


Figure 29: SER$_D$ determined using gravimetric tests for device 7:
2 tests, paper 0, type A 1m³ chamber

The TVOC emission rates determined within two days (Figure 30) showed a relatively good comparability. They are the highest TVOC emission rates determined within this project.

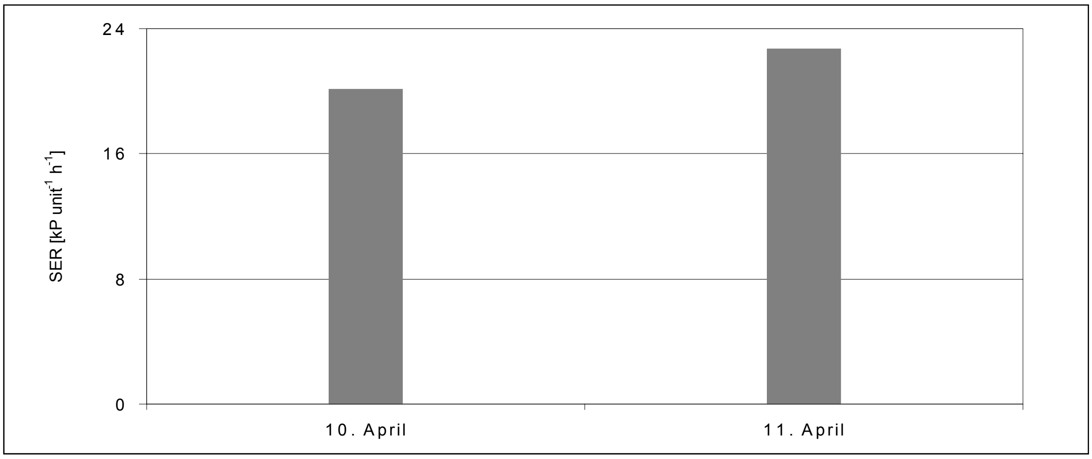


Figure 30: SER$_{TVOC}$ for device 7: 2 tests, paper 0, type A 1m³ chamber

Similarly to device 3, the main emissions were an unidentified compound and several alkanes ("alkane hill"), as well as heptene, styrene and xylenes, both in the printing and cold and standby phases.

Table 18: VOC emission rates [µg unit^{-1} h^{-1}] for device 7, second test

Substance	**Cold**		**Standby**		**Printing and follow-up phase**			
	C 1	**C 2**	**St 1**	**St 2**	**Pr 1***	**Pr 2***	**F***	**Pr 2**
Benzene	ND	**ND**	ND	**ND**	ND	**ND**	ND	**ND**
Heptene	177	**212**	283	**221**	1148	**2036**	872	**3605**
Toluene	15	**16**	19	**16**	112	**192**	48	**340**
Hexanal	ND	**ND**	ND	**ND**	24	**64**	20	**113**
Ethylbenzene	5	**6**	8	**6**	56	**136**	48	**241**
m,p-Xylene	11	**14**	19	**15**	152	**384**	136	**680**
Styrene	36	**49**	70	**55**	688	**1692**	568	**2996**
o-Xylene	4	**5**	6	**5**	60	**156**	72	**276**
Benzaldehyde	6	**7**	6	**5**	60	**144**	80	**255**
Phenol	3	**1**	3	**3**	8	**16**	108	**28**
Unidentified	17	**3**	31	**26**	2964	**6568**	2312	**11628**
Acetophenone	2	**3**	2	**2**	16	**40**	ND	**71**
Alkane hill	11	**19**	ND	**ND**	416	**1176**	468	**2082**
Nonanal	5	**4**	5	**4**	32	**ND**	ND	**ND**
Pentadecane	1	**1**	1	**1**	12	**ND**	12	**ND**
Hexadecane	1	**1**	1	**1**	20	**56**	ND	**99**
TVOC	294	**341**	454	**360**	5768	**12660**	4744	**22414**

Columns marked with * contain apparent emission rates, as the short printing time did not allow for an equilibrium to develop and/or the follow-up phase also failed to establish an equilibrium, thus concentrations were still decreasing. ND: Non-detectable

Ozone emission stayed below the detection limit during the printing process.

5.3.8 Device 8

Comparative measurements were performed on device 8 using recycling paper (P 0) in the three test chambers available.

A comparison of the results of the tests on recycled paper in the type A and B 1m³ chambers indicates that the SER_D values exhibit a moderate increasing tendency at a low level (Figure 31).

The gravimetric dust analysis in the 20m³ chamber shows a completely different picture. SER_D of 4.14 mg per unit and hour obtained in the test of 9th July is a markedly increased value in comparison with those of the type A and B 1m³ chambers under otherwise constant test conditions. An increased dust blank value in the 20m³ chamber was excluded by repetition measurements. The explanation given in connection with device 3 may apply to this behaviour.

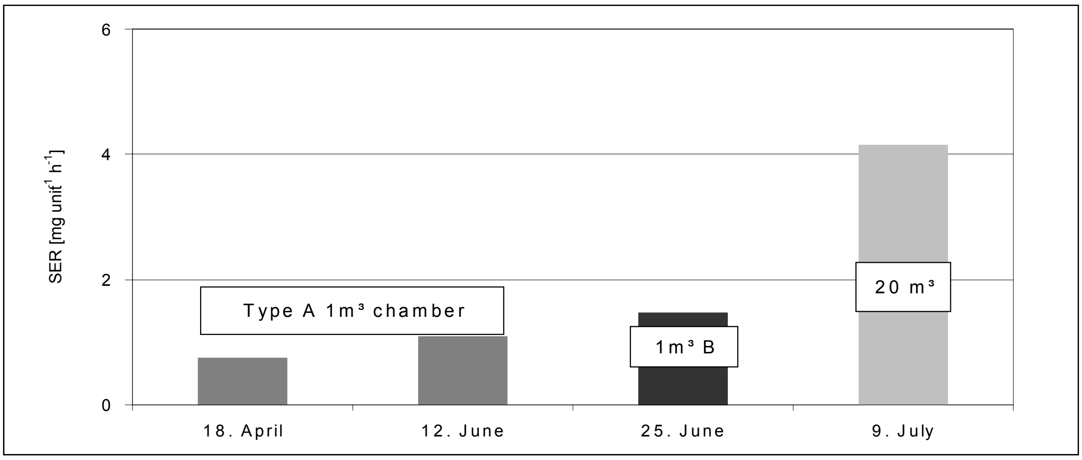


Figure 31: SER_D determined using gravimetric tests: device 8, 4 tests, paper 0

TVOC measurements displayed in Figure 32 show, like a large number of devices, a pronounced concentration decay as a function of time. Comparative measurements on the aged device in the 1m³ and 20m³ chambers at times near each other exhibited a good agreement.

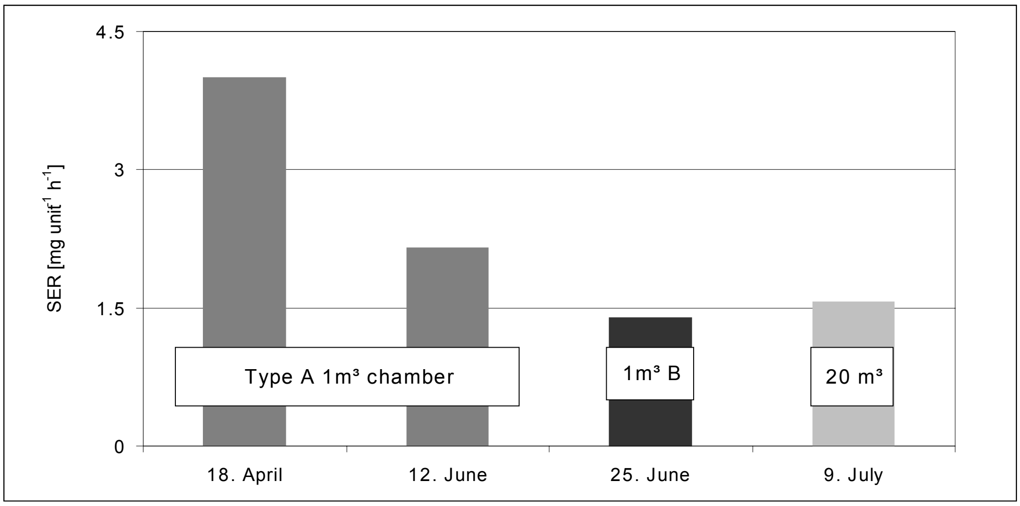


Figure 32: SER$_{TVOC}$ for device 8: 4 tests, paper 0

The main substances were xylenes, styrene, ethylbenzene and also benzaldehyde, acetophenone and hexanal, which, apart from hexanal, were also present both in the cold and standby phase, however in small concentrations, as indicated in Table 19.

Table 19: VOC emission rates [µg unit^{-1} h^{-1}] for device 8, first test

Substance	**Cold**		**Standby**		**Printing and follow-up phase**					
	C 1	**C 2**	**St 1**	**St 2**	**Pr 1***	**Pr 2***	**Pr 3***	**Pr 4***	**F***	**Pr 4**
Benzene	ND	**ND**	ND	**ND**	ND	ND	ND	ND	ND	**ND**
Toluene	2	**2**	2	**1**	ND	ND	20	12	ND	**16**
Hexanal	1	**ND**	ND	**ND**	ND	88	132	228	72	**305**
Ethylbenzene	4	**4**	5	**5**	64	160	220	356	112	**477**
m,p-Xylene	6	**5**	5	**5**	72	180	244	372	128	**498**
Styrene	4	**5**	10	**17**	80	180	248	404	144	**541**
Heptanal	ND	**ND**	ND	**ND**	16	24	24	48	16	**64**
o-Xylene	4	**3**	4	**4**	64	164	224	372	116	**498**
Benzaldehyde	8	**5**	5	**6**	84	164	212	308	92	**413**
Phenol	6	**8**	11	**14**	64	128	156	208	72	**279**
Ethylhexanol	3	**3**	2	**2**	12	28	32	52	16	**70**
Acetophenone	3	**2**	4	**3**	48	88	112	176	48	**236**
Nonanal	5	**4**	5	**5**	40	64	84	124	36	**166**
BHT	ND	**ND**	ND	**ND**	28	44	52	84	24	**113**
Pentadecane	1	**1**	1	**1**	24	60	80	108	28	**145**
Hexadecane	2	**1**	1	**1**	44	100	124	184	48	**247**
TVOC	49	**43**	55	**64**	640	1472	1964	3036	952	**4068**

Columns marked with * contain apparent emission rates, as the short printing time did not allow for an equilibrium to develop and/or the follow-up phase also failed to establish an equilibrium, thus concentrations were still decreasing. ND: Non-detectable

Ozone emission stayed below the detection limit during the printing process.

5.3.9 Device 9

Device 9 was investigated both in tests on recycled paper and comparative tests between the type B 1m³ chamber and the 20m³ chamber on new paper 1. 250 sheets were printed on 2nd December and 500 sheets on 3rd December in the type B 1m³ chamber. A comparison measurement took place in the 20 m³ chamber, likewise on 250 sheets on 10th December.

A comparison of the results of the tests in the type B 1m³ chamber indicates that the SER_D values shown in Figure 33 exhibit a significant decrease. This may however be explained, as with device 3, by the use of new paper (P 1) instead of recycled paper.

The gravimetric dust analysis in the 20m³ chamber shows a completely different picture. SER_D of 7.63 mg per unit and hour obtained in the test of 10th December is a markedly increased value in comparison with those of the type B 1m³ chamber under otherwise constant test conditions. An increased dust blank value in the 20m³ chamber was excluded by repetition measurements. The explanation given in connection with device 3 may apply to this behaviour.

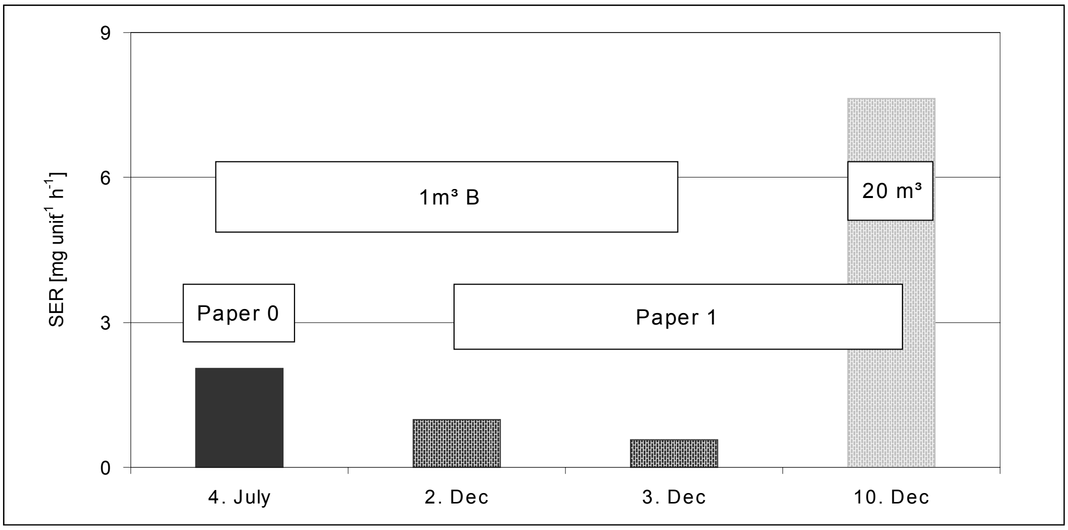


Figure 33: SER_D determined using gravimetric tests: device 9, 4 tests, papers 0 and 1

Ozone emission stayed below the detection limit during the printing process.

As Figure 34 indicates, TVOC emission rates calculated from the last printing phases show a very good agreement for the two different paper quantities (250 sheets on 2nd December and 500 sheets on 3rd December). The test in the 20m³ chamber yield a TVOC emission rate which is in good agreement with those measured in the type B 1m³ chamber. The main substances were xylene, styrene and ethylbenzene as shown in Table 20.

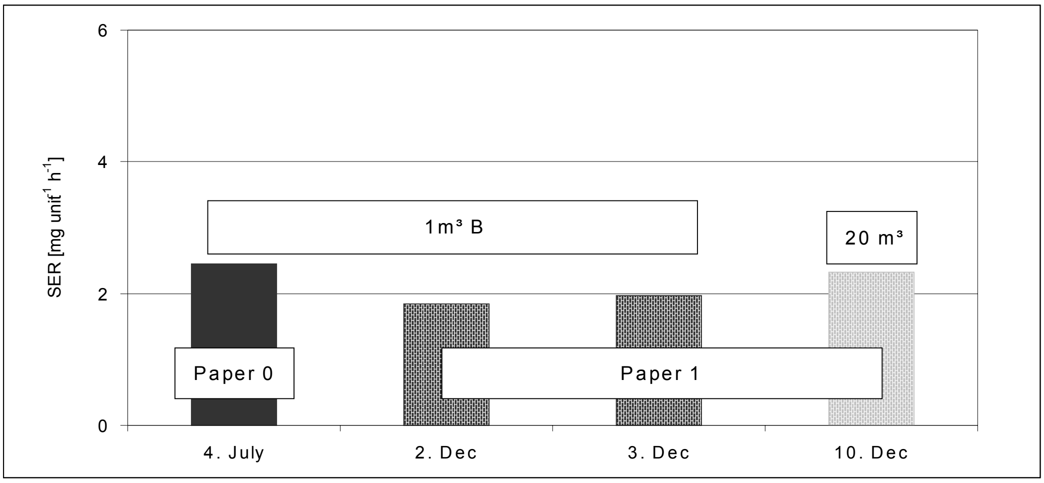


Figure 34: SER_{TVOC} for device 9: 4 tests, papers 0 and 1

Table 20: VOC emission rates [µg $unit^{-1}$ h^{-1}] for device 9, first test

Substance	Cold		Standby		Printing and follow-up phase					
	C 1	C 2	St 1	St 2	Pr 1*	Pr 2*	Pr 3*	Pr 4*	F*	Pr 4
Benzene	ND	**ND**	ND	**ND**	ND	ND	ND	ND	ND	**ND**
Toluene	2	**2**	1	**1**	9	18	40	22	9	**27**
Hexanal	ND	**ND**	ND	**ND**	18	57	88	101	31	**124**
Ethylbenzene	4	**5**	5	**5**	97	251	348	392	128	**478**
m,p-Xylene	3	**4**	4	**5**	97	251	348	392	132	**478**
Styrene	3	**5**	3	**4**	44	128	70	202	70	**247**
Heptanal	4	**5**	4	**ND**	62	79	ND	88	18	**107**
o-Xylene	2	**2**	2	**3**	66	172	238	268	233	**328**
Benzaldehyde	2	**2**	2	**2**	31	75	101	106	31	**129**
Phenol	6	**2**	7	**8**	31	35	57	31	18	**38**
Ethylhexanol	1	**1**	1	**1**	4	9	13	13	4	**16**
Acetophenone	1	**1**	1	**1**	22	53	66	75	22	**91**
Nonanal	2	**1**	1	**1**	13	35	44	48	18	**59**
BHT	ND	**ND**	ND	**ND**	13	31	35	40	13	**48**
Pentadecane	ND	**1**	ND	**ND**	22	62	79	75	22	**91**
Hexadecane	ND	**ND**	ND	**ND**	18	48	62	62	22	**75**
TVOC	30	**31**	ND	**31**	546	1302	1588	1914	770	**2337**

Columns marked with * contain apparent emission rates, as the short printing time did not allow for an equilibrium to develop and/or the follow-up phase also failed to establish an equilibrium, thus concentrations were still decreasing.
ND: Non-detectable

6 Investigations for method development

6.1 Climate

The first experiments for the test method development were carried out on printer 0 with recycled paper in the type B 1m³ chamber at an air exchange rate of 1 h^{-1}. Use of recycled paper was an initial default of the agency commissioning the project. Figure 35 illustrates the results of this test. Relative humidity rose to over 95% during printing as the printer rollers get heated up to about 180 °C during printing which caused water vapour condensation in the test chamber particularly in local cold spots such as the bottom of the chamber. This is the consequence of water evaporation from the recycled paper. Temperature images taken by an infrared camera clearly show the strong heat development. Figure 36 shows an example of an infrared picture of a paper during printing.

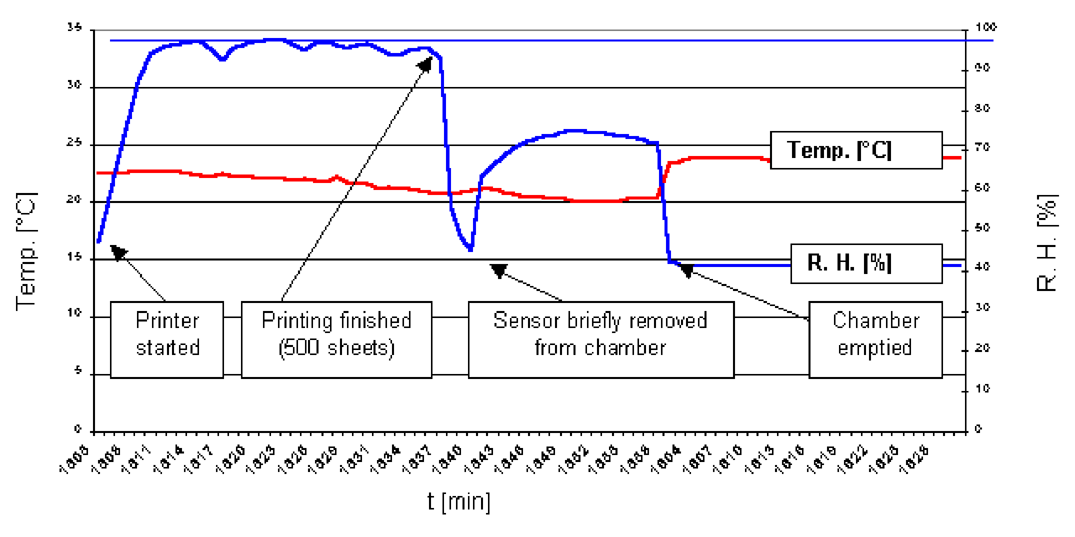


Figure 35: Printer 0, type B 1m³ chamber, air exchange rate n = 1 h-1, non-conditioned recycled paper

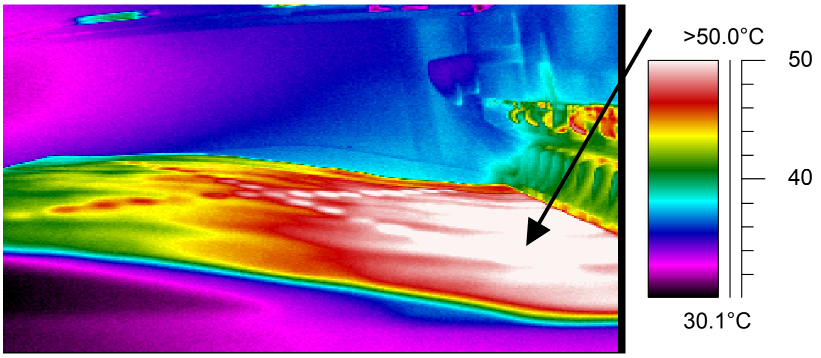


Figure 36: Infra red image of a sheet of paper being printed [right: paper ejection from printer, left: printed sheet (arrow)]

The test conditions were therefore changed and the recycled paper was first conditioned, i.e. pre-dried in a drying oven for 7 days at 50 °C. Air exchange rate was first maintained at $n = 1\ h^{-1}$. Figure 37 shows the results of this test. Relative humidity still increased to about 90% during printing and local water vapour condensation occurred in the test chamber.

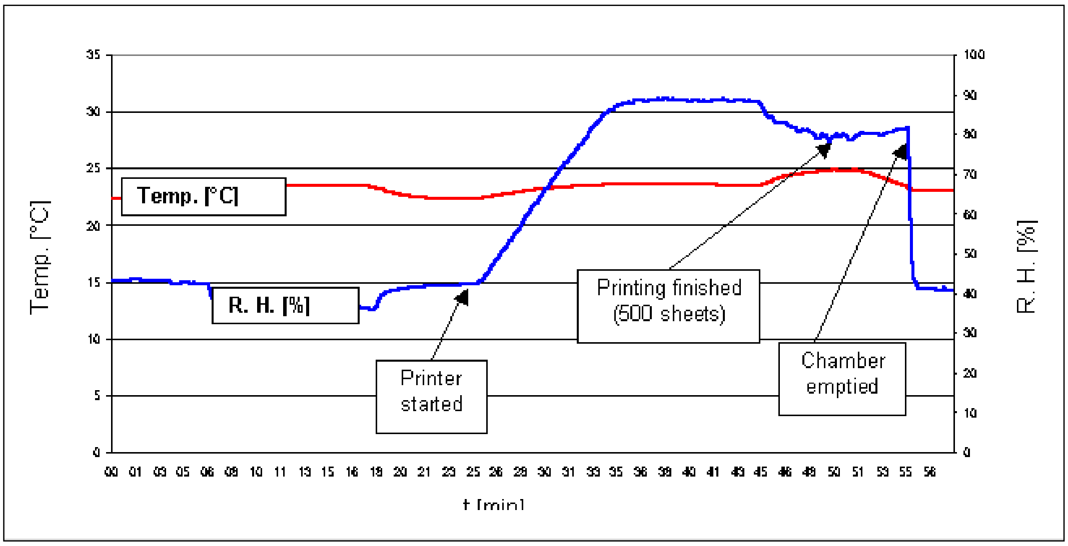


Figure 37: Printer 0, 1m³ chamber B, air exchange rate $n = 1\ h^{-1}$, dried recycled paper (50 °C / 7 days)

Figure 38 shows the results of another test on recycled unconditioned paper applying an air exchange rate of $5\ h^{-1}$. Relative humidity still rose to about 85% during printing and there was condensed water in a few places on the chamber bottom.

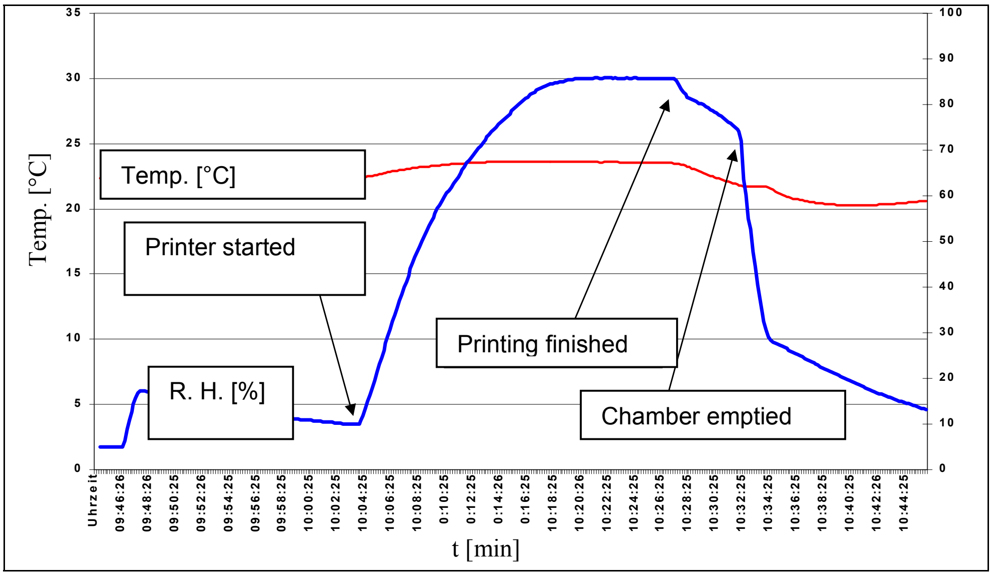


Figure 38: Printer 0, 1m³ chamber B, air exchange rate $n = 5\ h^{-1}$, non-dried recycled paper

In the last preliminary test (Figure 39) conditioned recycled paper and fivefold air exchange rate (n = 5 h^{-1}) was used. Relative humidity rose to only about 70% during printing and no water vapour condensation occurred in the test chamber.

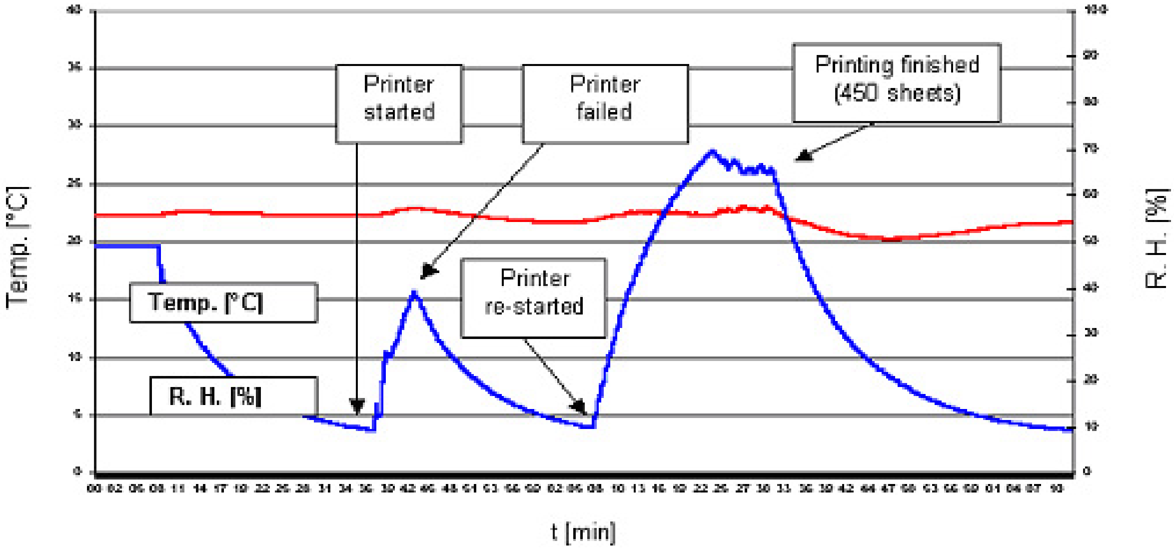


Figure 39: Printer 0, type B 1m³ chamber, air exchange rate n=5 h^{-1}, dried recycled paper (50 °C / 7 days)

Figure 40 shows the profile of ozone concentration as a function of time for the preliminary test device 0. It can be seen that opening the chamber caused an increase in ozone concentration. When the chamber was closed, the ozone measuring instrument indicated background noise only. An increase in ozone concentration during the subsequent tests in the type A and B 1m³ chambers could be reliably measured and unambigously assigned to the device.

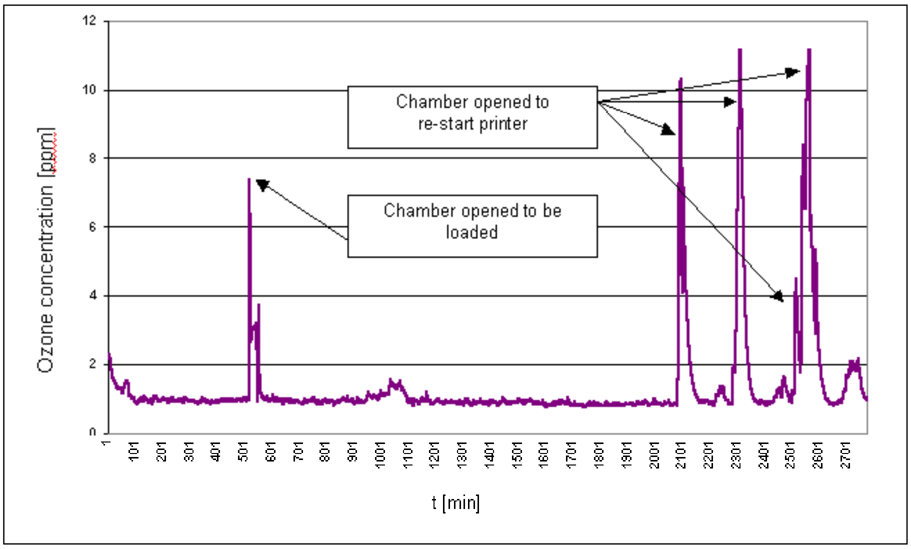


Figure 40: Printer 0, type B 1m³ chamber, ozone concentration profile as a function of time in ppm at n = 5 h^{-1}

After the preliminary tests were evaluated (see also 4.2.1 and 5.2) the following test conditions were specified for the type A and B 1m³ chambers:

- Use of new paper or pre-dried recycled paper
- Use of a high air exchange rate in small emission test chambers with a volume smaller or equal to 5 m³
- Use of dry supply air with a maximum 10 % R. H. at print start)

By adhering to these conditions for the subsequent device printing tests the relative humidity was maintained within a range of 60% to 70% (see Figure 39 and the climatic curves in the Appendix). The temperature was, depending on the chamber used, between 23 °C and 26 °C. These climatic problems did not arise in the 20m³ chamber.

6.2 Paper

The test chamber measurements found high concentrations of semivolatile organic compounds (SVOC) in comparison with the determined VOC concentrations, see also Paragraph 5.3.1. The paper used was one of the potential sources to be considered. In order to analyse possible emissions from the paper alone, the paper was tested using direct TDS (see 3.6.1). First the recycled paper used in the printer tests was investigated. Figure 41 shows the chromatogram obtained. This indicates that SVOCs found by the chamber tests originated from the paper used because peak pattern and identified individual substances showed a very good agreement with SVOCs obtained by chamber test (cf. Figure 17).

The deviation of climatic conditions from the standard conditions (23 C, 50 % R. H.), which arise during the printing process, in particular in small emission test chambers, appears acceptable for the following reason. High local temperatures of up to 180 °C in the printer or copier are most likely the main sources of VOC emissions, and the microclimate within the device deviates markedly from the conditions in the chamber anyway. The influence of the somewhat changing chamber conditions on the emission behaviour and the test result can therefore be regarded as negligible.

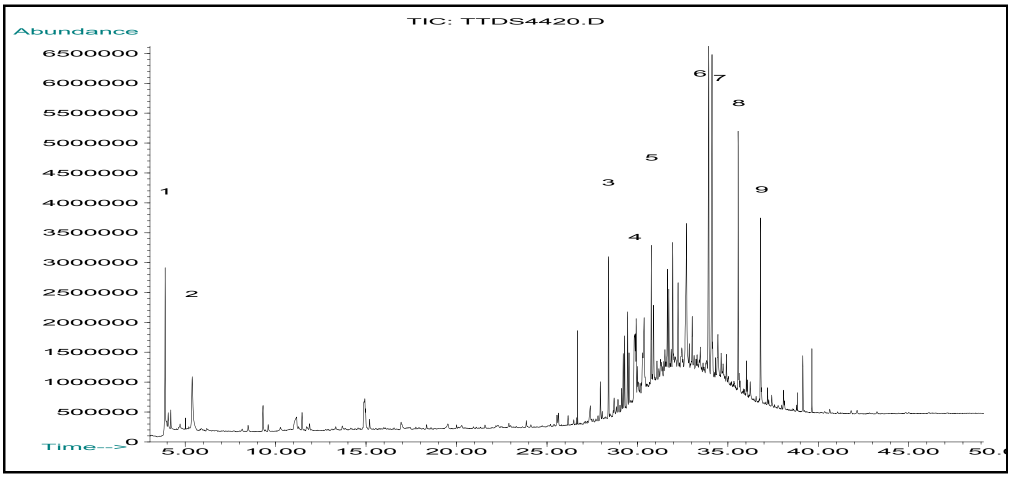


Figure 41: Chromatogram obtained by direct TDS of recycled papers used in test chamber measurements (1: acetic acid, 2: hexanal, 3: isopropyl-laurate, 4: diisopropylnaphthaline, 5: octadecane, 6: octadecene, 7: methyloleate, 8: eicosene, 9: docosene)

For comparison's sake new papers were also tested using direct TDS, a chromatogram example is shown in Figure 42. Altogether clearly less SVOCs were emitted from the new papers tested than from the recycled papers tested.

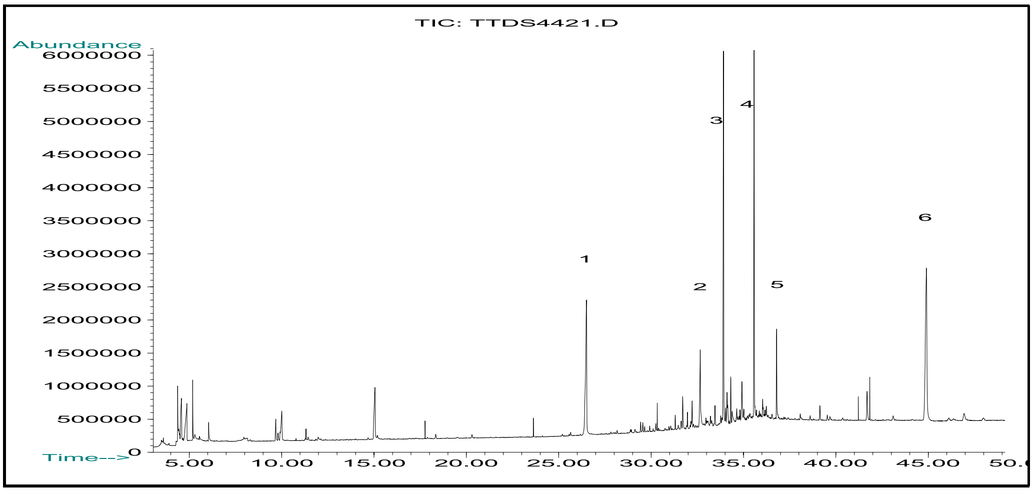


Figure 42: Chromatogram obtained by direct TDS of a new paper (1: orthohydroxybiphenyl, 2: hexadecanoic acid, 3: octadecene; 4 : eicosene, 5: docosene, 6: not identied)

6.3 Toners

All 32 toners, which had been made available, were tested using the methods described under 3.6.2. Table 21 shows the results for some selected compounds and the resulting sum of VOCs. The values were determined so that calibration was performed using compounds between d_6 benzene and n-propylbenzene. The sum in the last column refers only to the six explicitly mentioned components. Further components were proved using gas chromatography: they are displayed qualitatively in Table 23.

Table 21: General overview of all 32 toners tested

Sample	**Amount weighed [g]**	**Benzene [mg kg^{-1}]**	**Toluene [mg kg^{-1}]**	**p,m-Xylene [mg kg^{-1}]**	**o-Xylene [mg kg^{-1}]**	**n-Propylbenzene [mg kg^{-1}]**	**Styrene [mg kg^{-1}]**	**Sum [mg kg^{-1}]**
T-01	1.997	-	1.4	-	-	-	4.9	**6**
T-02	1.998	-	1.0	32	42	1.0	40	**120**
T-03	2.017	2.6	30	0.8	0.6	7.9	80	**120**
T-04	2.020	3.2	105	3.4	2.1	28	150	**290**
T-05	2.024	-	4.6	24	12	42	890	**970**
T-06	1.809	11	0.8	8.0	8.0	31	180	**240**
T-07	2.003	-	0.5	-	-	-	19	**20**
T-08	2.019	28	-	7.6	2.6	14	31	**80**
T-09	2.000	0.2	-	0.3	-	-	56	**60**
T-10	1.958	15	0.5	2.6	2.7	10	77	**110**
T-11	2.095	4.2	180	4.5	3.1	37	110	**340**
T-12	2.075	-	-	-	-	-	0.7	**1**
T-13	2.101	-	-	22	20	5.6	35	**80**
T-14	2.138	-	-	-	-	2.3	7.5	**10**
T-15	2.076	-	0.4	-	-	0.9	1.0	**2**
T-16	1.969	12	1.7	23	19	15	970	**1040**
T-17	1.890	13	1.0	22	18	16	1000	**1070**
T-18	1.993	-	0.4	-	-	-	1.2	**2**
T-19	1.986	-	0.3	-	-	-	-	**0.3**
T-20	2.020	-	1.4	-	-	-	25	**30**
T-21	1.945	-	0.8	-	-	-	-	**1**
T-22	2.037	1.9	5.0	0.7	1.1	3.5	17	**30**
T-23	1.397	-	1.3	8.6	14	-	20	**40**
T-24	2.014	0.2	0.4	13	10	2.1	27	**50**
T-25	1.965	-	0.7	6.1	11	-	25	**40**
T-26	2.132	-	-	6.0	6.4	1.4	24	**40**
T-27	1.937	-	0.9	0.8	-	-	2.2	**4**
T-28	1.781	-	0.6	-	-	-	0.6	**1**
T-29	1.934	-	2.2	10	6.0	1.7	20	**40**
T-30	2.028	-	-	-	-	-	-	
T-31	1.866	-	-	31	20	1.6	41	**90**
T-32	1.986	-	4.9	13	9.0	-	36	**60**

-: Non-detectable (under the detection limit of approx. 0.1 mg/kg)
(Components benzene, toluene, xylenes, n-propylbenzene were calibrated using d_6 benzene as an internal standard, styrene was evaluated using d_8 styrene)

Based on the results illustrated in Table 21, six different toners were selected for the co-operative test of the headspace method. The complete range of the detected concentrations was considered. Percentile values of the toners are displayed in Table 22.

Table 22: Percentile values of toners taken from Table 21

Percentile	95.	90.	75.	50.	25.
Concentration [mg kg^{-1}]	1005	340	115	40	8.15

Table 23 displays further compounds which were found in the toners. These compounds were not all quantified individually since they only sporadically occurred in the toners. The compounds in the list have not been completely checked via a retention time comparison using standard compounds but are in some cases the only plausible results of a database survey. The mass spectrum of a component, which was not found in any of the databases but occurred frequently, in some cases as the main component is shown in Figure 43.

Table 23: Further compounds from headspace tests of the toners which were not quantified, but exhibited high peaks

Sample	Additional components
T-01	Siloxane, benzochinon (small amount)
T-22	Ethylbenzene, 1-butanol, diethylbenzene, siloxane, methylisobutylketone, benzaldehyde,
T-02	1-Butanol, ethylbenzene, benzaldehyde, acetophenone
T-03	Unk. comp., ethylbenzene, 1-butanol, benzaldehyde, siloxane, 1-butanol
T-04	Ethylbenzene
T-05	Unk. comp.
T-06	Ethylbenzene, ethylhexanol, benzaldehyde, ethylhexylacetate
T-08	1-Butanol, benzaldehyde, ethylbenzene, diethylbenzene, ethoxyethanol, n-butylether
T-09	Methylisobutylketone, 1-butanol, benzaldehyde, siloxane
T-10	1-Butanol, benzaldehyde, ethylbenzene, diethylbenzene, ethylhexanol, ethylhexylacetate, n-butylether
T-11	Ethylbenzene, unk. comp. (main component)
T-12	Siloxane

Sample	Additional components
T-13	Ethylbenzene, 1-butanol, decane, dodecane, α-methylstyrene
T-14	Ethylbenzene, n-butylether, decane, dodecane, 1-octanol, unk. comp.
T-15	Dodecane, 1-octanol, unk. comp.
T-16	Ethylbenzene, n-butylether, benzaldehyde, propenoic acid butylether
T-17	Ethylbenzene, n-butylether, benzaldehyde, propenoic acid butylether
T-18	Siloxane, benzochinon
T-19	2-Butanon, methylisobutylketone
T-23	1-Butanol, benzaldehyde, ethylbenzene, acetophenone
T-24	Ethylbenzene, 1-butanol, benzaldehyde, acetophenone
T-25	1-Butanol, siloxane, benzaldehyde, ethylbenzene
T-26	Ethylbenzene, 1-butanol, benzaldehyde, acetophenone
T-27	Siloxane
T-28	Siloxane
T-29	1-Butanol, siloxane, ethylbenzene, unk. comp., trimethylcyclohexanon
T-30	Siloxane
T-31	Highly fluorinated hexanes, ethylbenzene, tributylamin (?), trimethylcyclohexanon
T-32	Ethylbenzene, methylisobutylketone

unk. comp. = unknown compound, presumably ether or ester (s. Figure 43)

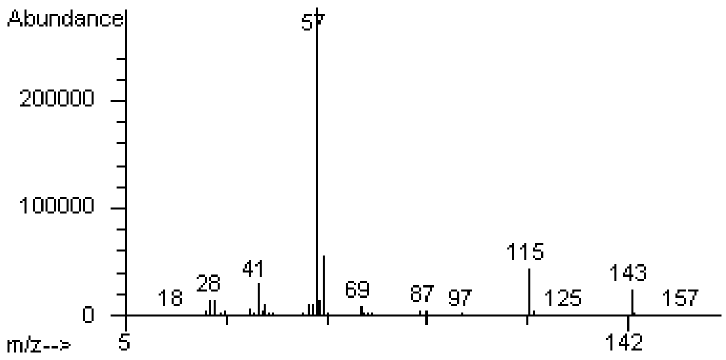


Figure 43: Chromatogram of a non-identified compound detected frequently in toners (possibly an ester or ether)

6.4 Testing ageing behaviour of selected devices

The results of the emission tests were already discussed in detail in Chapter 5. The “ageing behaviour” of the devices will be dealt with in this chapter.

Repetition tests were performed on devices 3, 4 and 8 under constant test conditions. The aim of the co-operative test was to clarify possible "aging behaviour" of the devices tested due to material ageing, transport or toner loss for example. Ageing and long-term emission behaviour is of great interest for an evaluation of the long-term impact of indoor air.

TVOC

TVOC emission rate of devices 3, 4 and 8 is illustrated as a function of time in Figure 44.

The tests from 12 March to 20 June show a constant TVOC emission rate for device 3. Considering the individual VOCs, a decrease in the emission rate of the volatile substances, e.g. xylene and styrene was observed. As far as the TVOC emission rate is concerned, this decrease was compensated for by the height of the "alkane hill" and the unidentified substance which remained constant. A marked decrease in the TVOC emission rate was observed for device 4 in the period between 14 March and 3 July. Device 8 showed a similar behaviour during the period from 18 April to 25 June.

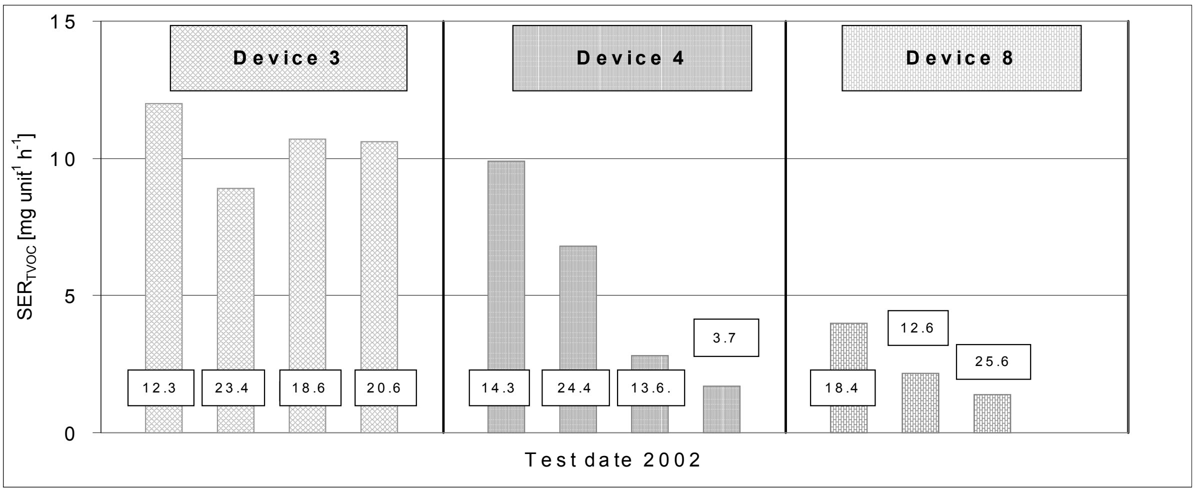


Figure 44: SER$_{TVOC}$ for devices 3, 4 and 8 as a function of time

<u>Ozone and dust</u>

In contrast to the TVOC emission rate, ozone emission rate measured on devices 3 and 4 (Figure 45) did not show any clear ageing effect in the period of March to Septembers and March to July.

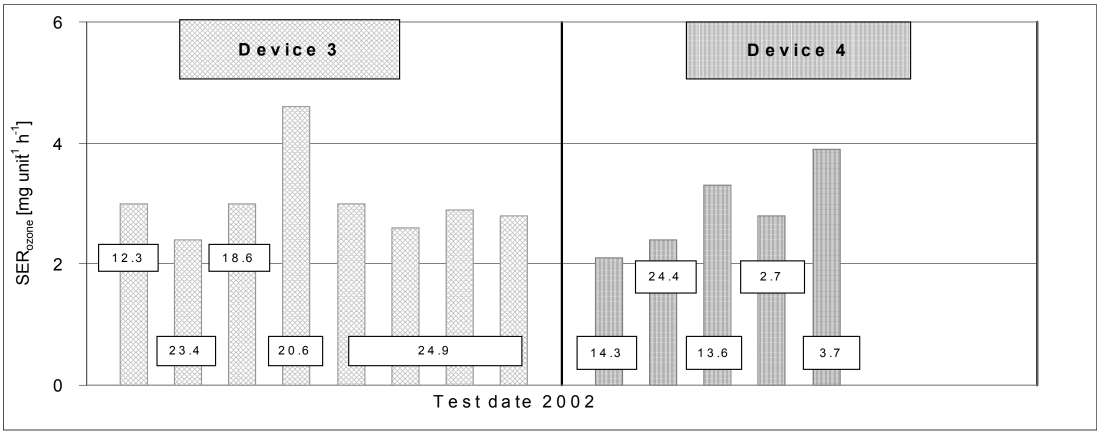


Figure 45: SER$_{ozone}$ for devices 3 and 4 as a function of time

Dust emission rates of devices 3, 4 and 8 are illustrated as a function of time in Figure 46.

Dust emission rates of device 3 analysed using gravimetric methods proved to be relatively constant in course of the period from March to June. Device 4 however showed a clear decrease in the course of the tests from March to July, while dust emission rates of device 8 determined using gravimetric method were increasing.

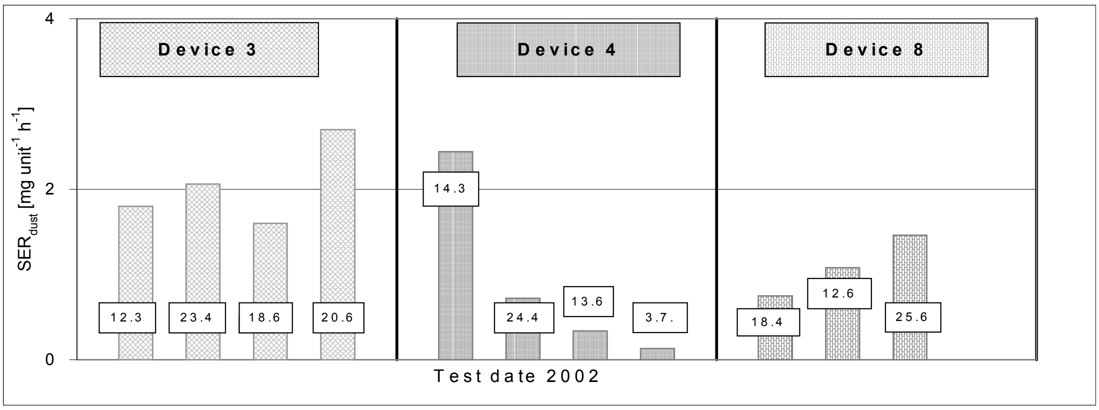


Figure 46: SER$_D$ for devices 3, 4 and 8 as a function of time

6.5 Comparison of measurements in various test chambers

Two 1m³ chambers (type A and B) and a 20m³ chamber were used (see Chapter 3.1). Devices 4 and 8 were tested in all three chambers with recycled paper. Only one comparison was possible for device 3 between the two 1m³ chambers (type A and B).

TVOC

Figure 47 shows a comparison of TVOC emission rates for devices 3, 4 and 8.

Test results on device 3 in both 1m³ chambers agree very well. The TVOC emission rate for device 4 determined in the type B 1m³ chamber equals 60 % of the value in the type A chamber. The TVOC emission rate measured in the 20m³ chamber is in very good agreement with the value of chamber A. However, the measured air concentrations of the individual substances in the 20m³ chamber were in some cases only just above the detection limit and may have been subject to a large error. The values of the type B 1m³ chamber and the 20m³ chamber for device 8 are in good agreement, but a 50% higher TVOC emission rate was found in type A 1m³ chamber.

It has to be born in mind as far as these chamber comparisons are concerned that the devices exhibit a pronounced ageing behaviour (cf. Chapter 6.4), so that a comparability, which looks less good at first sight, may be due to this effect.

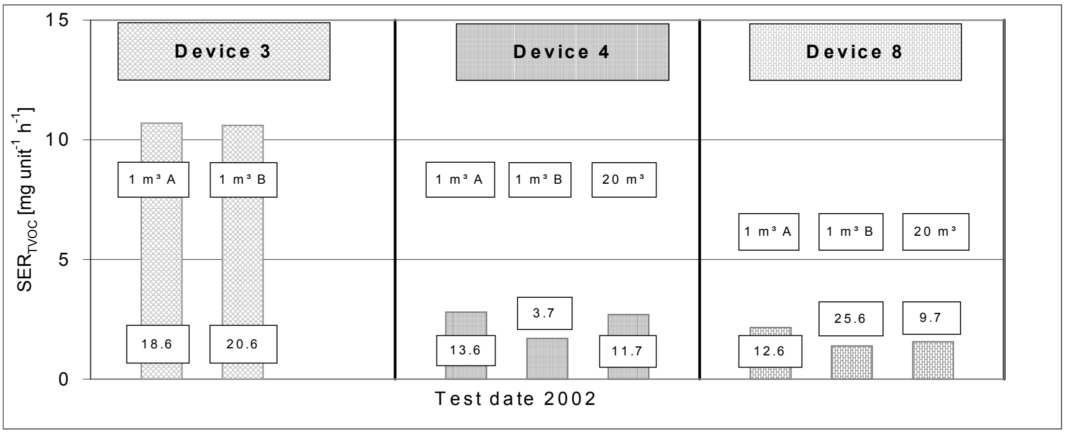


Figure 47: SER$_{TVOC}$ for devices 3, 4 and 8 comparing the chambers

Ozone

Ozone emission rates for device 3 and device 4 in the three test chambers used are displayed in Figure 48. Comparability and repeatability can altogether be considered very good.

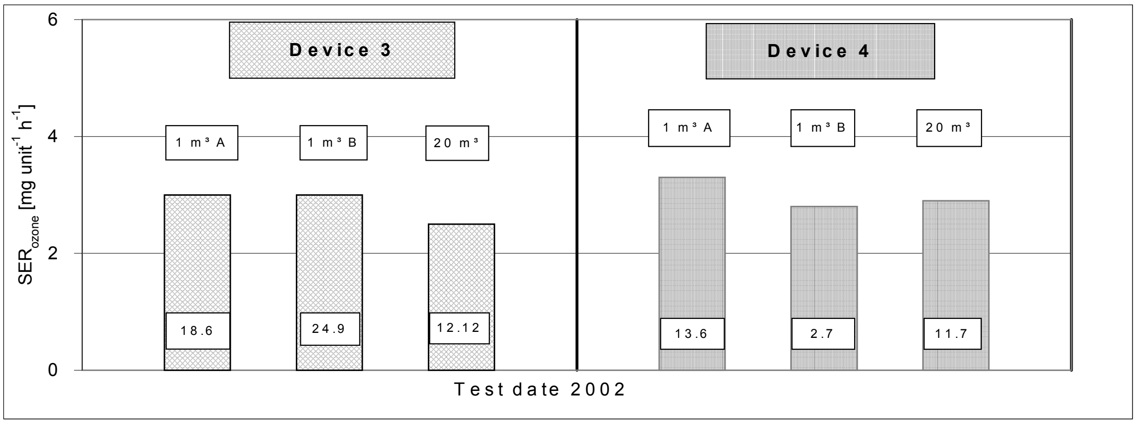


Figure 48: SER$_{ozone}$ for devices 3 and 4 comparing the chambers

Dust

Figure 49 illustrates a comparison of dust emissions for devices 3, 4 and 8.

It seems to apply to all devices that dust emission rates calculated for the 20m³ chamber is considerably higher than those in type A and B 1m³ chambers.

The way of sampling in the 20m³ chamber seems to be the reason for this. In the 20m³ chamber dust sampling was performed near the device as this is described in the ECMA standard 328 [18]. Obviously, increases in local concentration may occur depending on the exhaust air flow of the device since air is sometimes not sufficiently mixed near the device and in some cases the exhaust air flow has not been diluted by the test chamber air.

The results of three devices tested in comparison prove these statements.

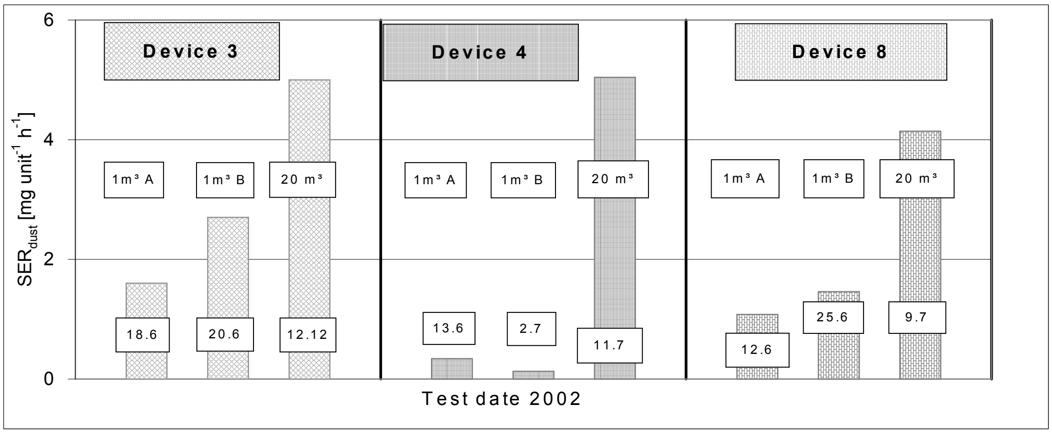


Figure 49: SER$_D$ for devices 3, 4 and 8 comparing the chambers

6.6 Influence of the number of printed sheets on emission rates

A special comparative test was undertaken on devices 3 and 9 in December 2002, where the number of printed sheets was varied. In addition, investigations took place in the type A 1m³ chamber and in the 20m³ chamber. The tests were performed on new paper 1. The results of these tests are summed up in the following. In addition, TVOC emission rate was calculated using different methods. This comparison is explained in Section 6.7.

Figure 50 shows the TVOC emission rates for devices 3 and 9 calculated from the printing and follow-up phases. The comparison shows a very good agreement for device 9 both for 250 and 500 printed sheets irrespective of the volume of the test chamber used. The values of device 3 differ somewhat more widely. This is probably due to a repair of the device which took place in the meantime and has led to a change of the VOC emission behaviour (see Section 5.3.3).

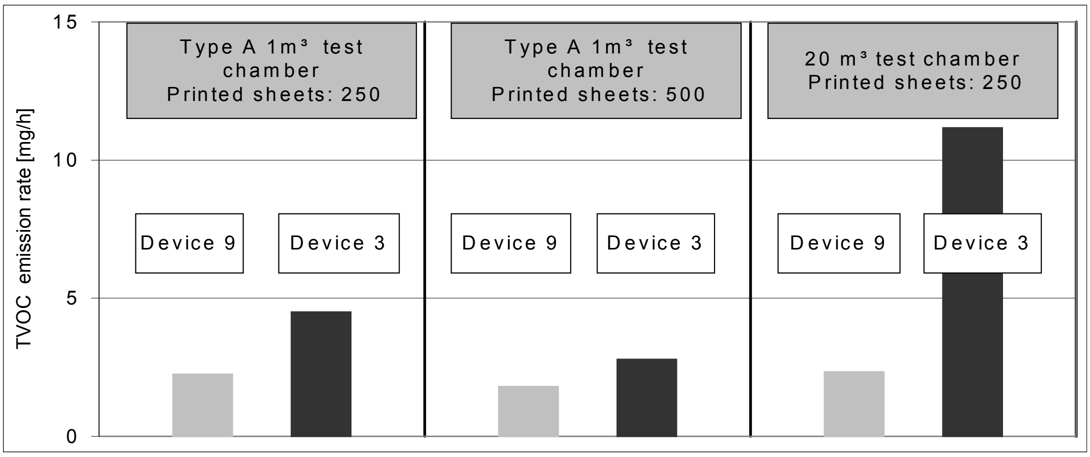


Figure 50: SER_{TVOC} for devices 3 and 9 comparing various test chambers and different numbers of printed sheets

Figure 51 shows ozone emission rates determined for the devices 3 and 9. The comparison shows a very good agreement for device 3 both for 250 and 500 printed sheets independently of the volume of the test chamber used. No ozone emission was detected for device 9.

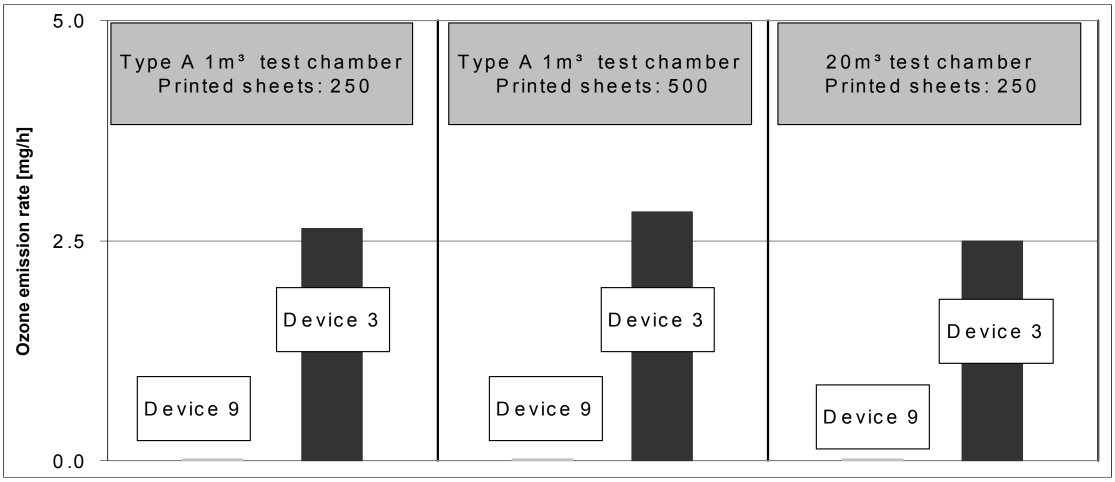


Figure 51: SER_{ozone} for devices 3 and 9 comparing various test chambers and different numbers of printed sheets

Figure 52 displays dust emission rates for devices 3 and 9. Comparability of dust emission rates between 250 and 500 printed sheets can be considered as good in view of the low measured values in the type A 1m³ chamber. The problem of the disproportionately high dust emission rates in the 20m³ chamber has been already discussed several times, particularly in Chapters 5.3.3 and 6.5.

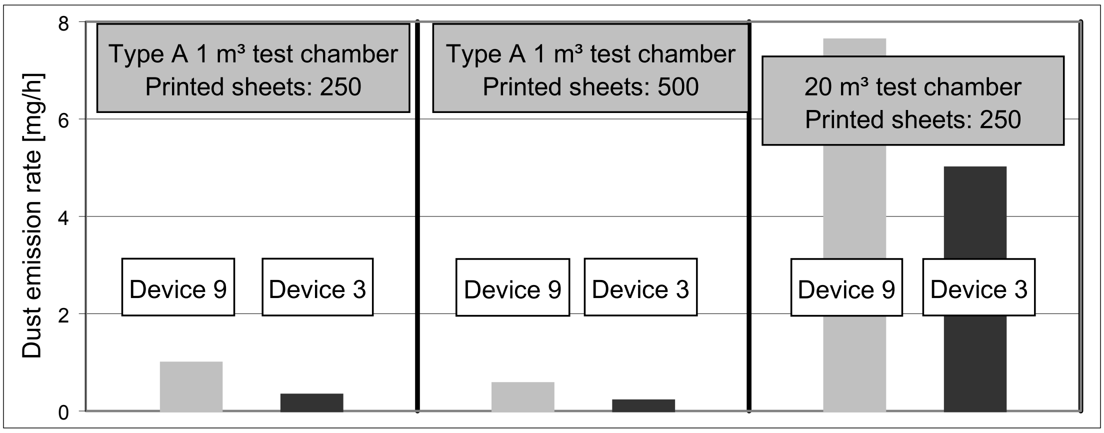


Figure 52: SER_D for devices 3 and 9 comparing various test chambers and different numbers of printed sheets

6.7 Comparison of various calculation methods on SER_{TVOC}

The TVOC emission rate was determined at the same time for some tests using different calculation methods. Figure 53 illustrates the TVOC emission rates for devices 3 and 9 related to the type A 1m³ chamber. On the one hand SER_{TVOC} was determined during the last printing phase (symbol "Pr" in Figure 53), on the other hand from the entire printing and follow-up phase (symbol "PrF" in Figure 53). The formulas used are summed up in Chapter 3.5. The comparison shows a very good agreement for device 9 both for 250 and for 500 printed sheets. The values differ somewhat more widely for device 3. This is probable due to the repair of the device performed in the meantime, which has led to a change in the VOC emission behaviour.

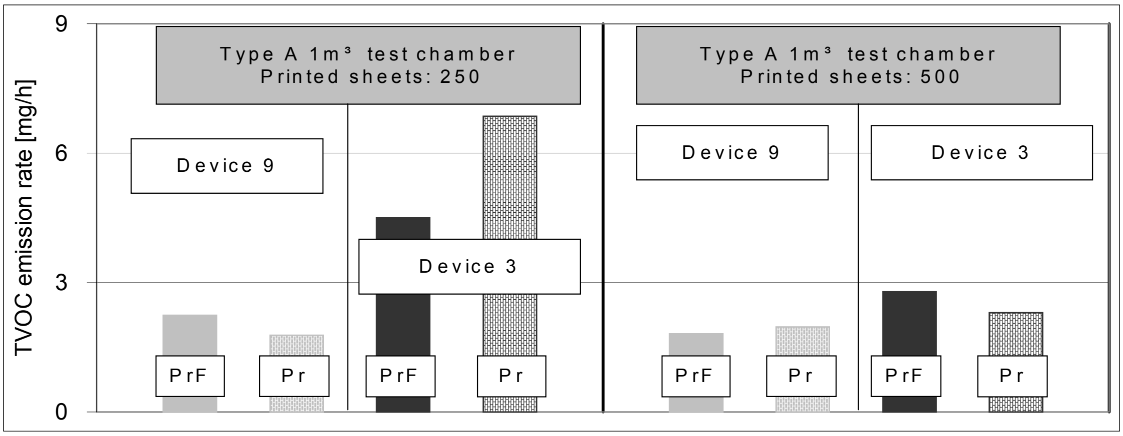


Figure 53: SER_{TVOC} for devices 3 and 9 comparing different numbers of printed sheets and various calculation methods

6.8 Particle count

The toxicological relevance of ultrafine aerosols is increasingly questioned in recent time since these seem to have a stronger biological effectiveness than larger particles with the same mass concentration [24], [7], [64]. In [56] and [55] some still unresolved questions are raised concerning particle emissions: "Since nothing confirmed is known of the damage mechanisms it is not clear which parameters should be tested in the working place. Is it the particle concentration, the surface concentration, or - less probably - the mass concentration?… "[56].

Additional tests were carried out using a particle counter within the framework of this research project on the emission behaviour of hardcopy devices. The sampling took place within the emission test chambers. The air sucked in was led to the measuring instrument standing outside of the chambers by about a 0.5 metres long hose. Sampling for the gravimetric dust analysis and the particle counting took place in the 20m³ chamber in almost the same place near the device tested in accordance with the ECMA standard 328. Sampling for the gravimetric dust analysis in the type A and B 1m³ chambers was performed outside at the chamber wall. All particle emission rates indicated in the following refer to the particle sizes smaller than 0.1 to 10 µm.

Ultrafine particles are dust, smoke and fog, whose particles are smaller than 100 nm (0.1 µm) [56]. The smallest measurable size class of the particle counter available was smaller than 0.1 to 1 µm. The ultrafine particles are only partially contained in this. Therefore the results of the investigations can here only provide a first reference to the emission behaviour of hardcopy devices concerning ultrafine particles. However, since interesting results were obtained, the results of particle measurement are summarised here. If these parameters are to be included into a follow-up evaluation further investigations are required since it was not possible to examine the ultrafine particles in greater detail within the framework of this research project due to aspects of measurement technology.

Figure 54 illustrates a typical particle counter result for the size class smaller than 0.1 to 1.0 µm over the entire test cycle by the example of device 3. Each opening of the test chamber causes a signal. It can be clearly seen that particle emission rises significantly during the actual printing process.

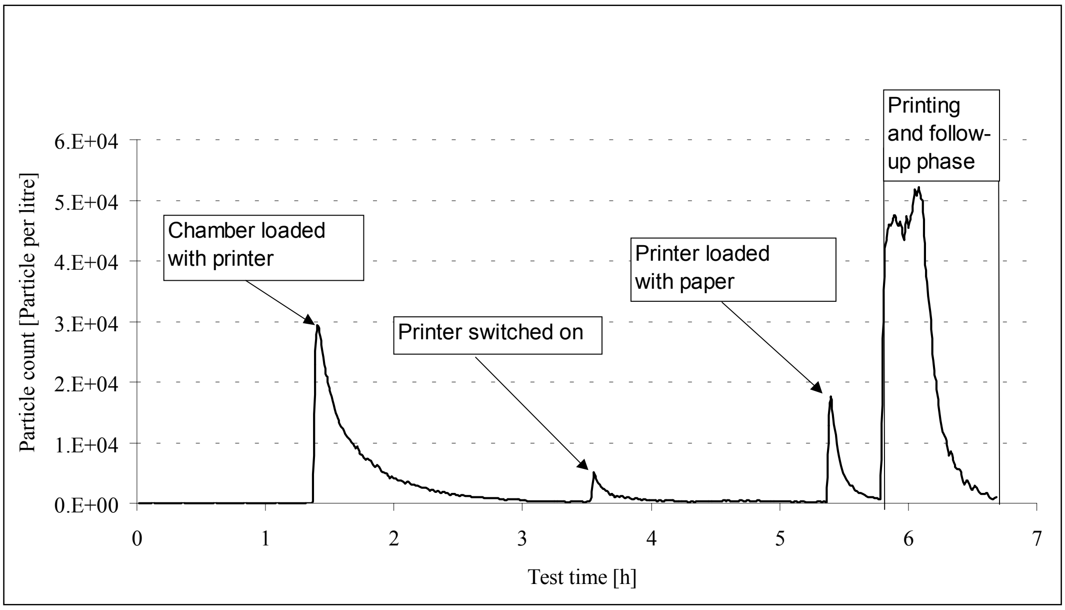


Figure 54: Typical particle counter result for the size class < 0.1 to 1.0 µm over the entire test cycle (device 3 in the type A 1m³ chamber)

The calculated particle emission rates for all tests performed are displayed in Table 30 in the Appendix. It is now the intention to perform a first weighting for the received results and to clarify some interesting aspects. The particle emission rates for device 1, determined under the most diverse test conditions, are plotted in Figure 55 as an example. Interestingly enough the highest particle emission rates were determined when sheets of empty recycling paper were printed. In addition, an increase of the black coverage of paper 4 (P 4) from 5 % (standard) to 20 % led to an increase in the particle emission rate.

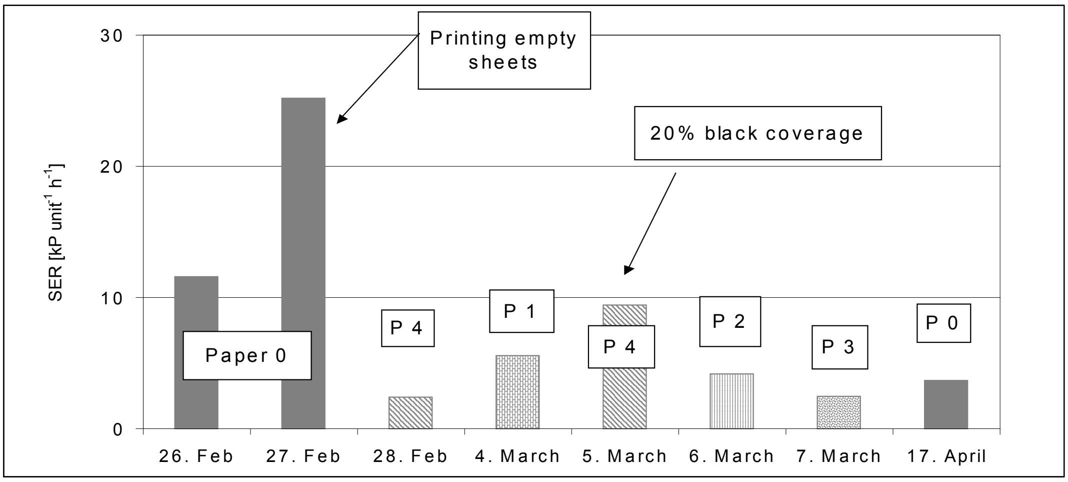


Figure 55: Particle emission rates for device 1: 8 tests, 5 sorts of paper, type A 1 m³ chamber

Figure 56 shows an overview of the particle emission rates determined for all devices tested under comparable test conditions. The test figures indicate that there are obviously devices which exhibit rather low particle emissions by comparison. The differences are in certain cases considerable.

Comparing the dust emission rates indicated in Chapter 5 “Results of emission tests” determined using gravimetric methods with the appropriate particle emission rates, it can be seen that only a partial correlation exists between the high dust emission rates determined gravimetrically and the particle emission rate. Further investigation is needed to describe this connection more precisely.

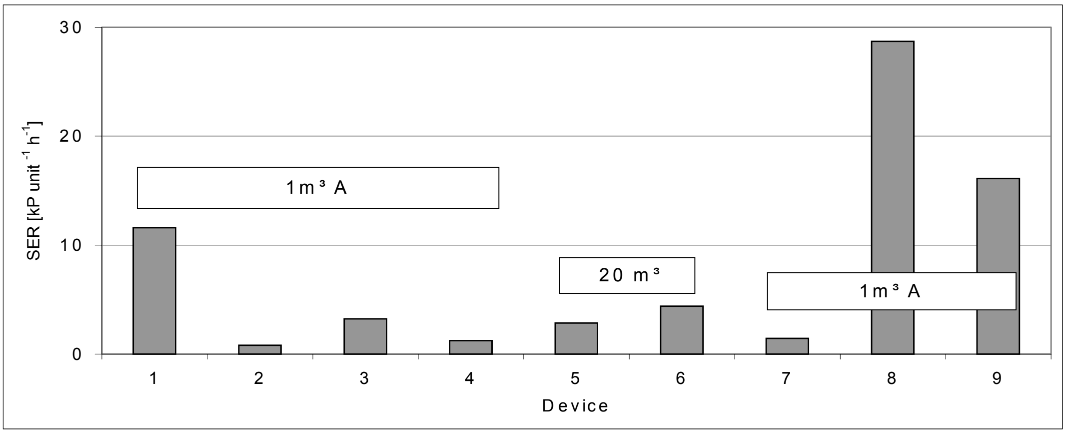


Figure 56: Overview of particle emission rate on recycled paper for all devices tested

The following circumstances can be derived from the measurements with certainty. Particles are emitted in each printing process. It can only be guessed to which extent they are emitted from the paper, the toner or the device itself. The smaller their size, the larger the number of the emitted particles. Since relatively little is known about the effects of these small particles, health impairment cannot to be excluded and further investigations may be necessary.

7 Co-operative tests

7.1 VOC, dust and ozone emission tests

VOC, ozone and dust emissions of four selected printers were measured in a co-operative test involving four testing institutes (BAM, LGA, BIA and Sony). After the first test in BAM the devices were transported by a BAM vehicle to the first testing institute. After 2 weeks the devices were returned to BAM and tested there again. The devices were then transported to the second testing institute, from there to the third testing institute and afterwards returned to BAM.

Due to the test chamber sizes it was not possible for every institute to test all devices. In one of the institutes there were difficulties in preparing the test chamber, so that only one device was tested within the framework of the co-operative test. Another testing institute performed the VOC tests on only two devices and was not able to check the air exchange rate of the test chamber. The emission rates were therefore calculated from the measured concentrations with the maximum air exchange rate of 8 h^{-1} declared by the test chamber manufacturer.

The following tables summarize the emission rates in µg per hour and the devices for selected VOCs (target substances for the co-operative test).

Table 24: Comparison of emission rates of the last printing phase for device 1

Substance	Institute 1	Institute 2	Institute 4
Benzene	ND	6	ND
Toluene	64	14	26
Hexanal	228	ND	ND
Ethylbenzene	124	195	167
o, m, p-Xylene	328	435	418
Styrene	180	230	242
Sum	924	874	853

ND: Non-detectable

Table 25: Comparison of emission rates of the last printing phase for device 3

Substance	Institut 1	Institut 2	Institut 4
Benzene	ND	17	n.n.
Toluene	40	ND	45
Hexanal	320	ND	ND
Ethylbenzene	156	60	56
o, m, p- Xylene	104	41	59
Styrene	68	46	54
Sum	688	147	214

ND: Non-detectable

Table 26: Comparison of emission rates of the last printing phase for device 4

Substance	Institute 1	Institute 2
Benzene	ND	ND
Toluene	5852	6065
Hexanal	88	26
Ethylbenzene	444	385
o, m, p- Xylene	508	415
Styrene	712	600
Sum	7604	7491

ND: Non-detectable

Institute 1 was only able to prove concentrations of 2 µg m^{-3} for some of the target substances for device 6 tested by institutes 1, 2 and 3. Institute 2 and 4 was not able to prove any of the substances (detection limit 2 and 5 µg m^{-3}).

The results of a maximum of three testing institutes participating in the co-operative test are not satisfactory to allow calculation of an average value of the results and a standard deviation as normal for statistics purposes.

A comparison of the results for device 4 shows a very good agreement of the measured values for the individual substances and their sum.

For device 1 the overall values of the three testing institutes likewise indicate a very good agreement, although the measured values of the single substances are in some cases very different. Thus hexanal was not found by Institutes 2 and 4, while Institute 1 considered it the main component. Benzene was found by Institute 2 only.

The values for ethylbenzene, xylenes and styrene measured by Institute 1 are smaller than those of the other two institutes. This opposes the results for device 3, for which Institute 1 showed these substances to be somewhat greater. Hexanal was also found here by Institute 1 only. Benzene was detected by Institut 2 only, however they failed to find toluene. On the other hand, the results of Institutes 1 and 4 exhibit a very good agreement. Among the test results of device 3, VOC values show the biggest differences between various testing institutes.

Two institutes participated in the comparative tests of dust and ozone emission rates for four different hardcopy devices. The measurement of Institute 2 was temporally limited by the repetition tests of Institute 1. Table 27 displays a comparison of the test results. Since only two testing institutes participated in the comparative tests, the significance of the results is not particularly high and the results have to be used with care.

Table 27: Comparison of dust and ozone emission rates [mg h^{-1}], measured in Institutes 1 and 2

Device	Substance [mg h^{-1}]	Institute 1	Institute 2	Institute 1
1	Ozone	< 0.02	0.32	< 0.02
	Dust	2.20	1.02	0.90
3	Ozone	3.00	3.40	2.40
	Dust	1.80	0.11	2.06
4	Ozone	2.10	2.70	2.40
	Dust	2.44	0.07	0.72
6	Ozone	< 0.02	0.25	< 0.02
	Dust	1.16	0.37	1.81

It can be stated qualitatively that ozone emission rates determined by both institutes show a relatively good agreement. Test results on devices with significant ozone emissions are very close to each other. Institute 1 found the ozone emission rates for devices with very low ozone emission to be below the detection limit, while Institute 2 did measure (low) ozone emission rates. The measured dust emission rates of one of the devices compared relatively well, the other three devices exhibited large differences. The dust emission rates found by Institute 2 for these three devices might be near to the determination limit of the gravimetric dust analysis procedure.

7.2 Toner tests

Six of the 32 toners described under 6.3 were tested by a co-operative test with 4 institutes participating. It was intended to carry out the measurements, as far as possible, using the same method which was made available to the participants. However due to apparatus conditions, two of the participants (Institutes 3 & 4) deviated from this and those two institutes (1 & 2) who did use the procedure described in 3.6.2, made the evaluation from ethylbenzene using d_9 styrene, which rather overestimates the overall values (see Figure 57). One the other institutes (No. 3) desorbed the toners thermally using a dynamic system which collected the eluate on Tenax and then undertook the analysis. Though Institute 4 also used a static headspace method, the toners were covered with a semivolatile solvent (dimethylacetamide) and heated afterwards only. Figures 57, 58 and 59 show relatively good agreement of the results despite fairly large differences in the methods.

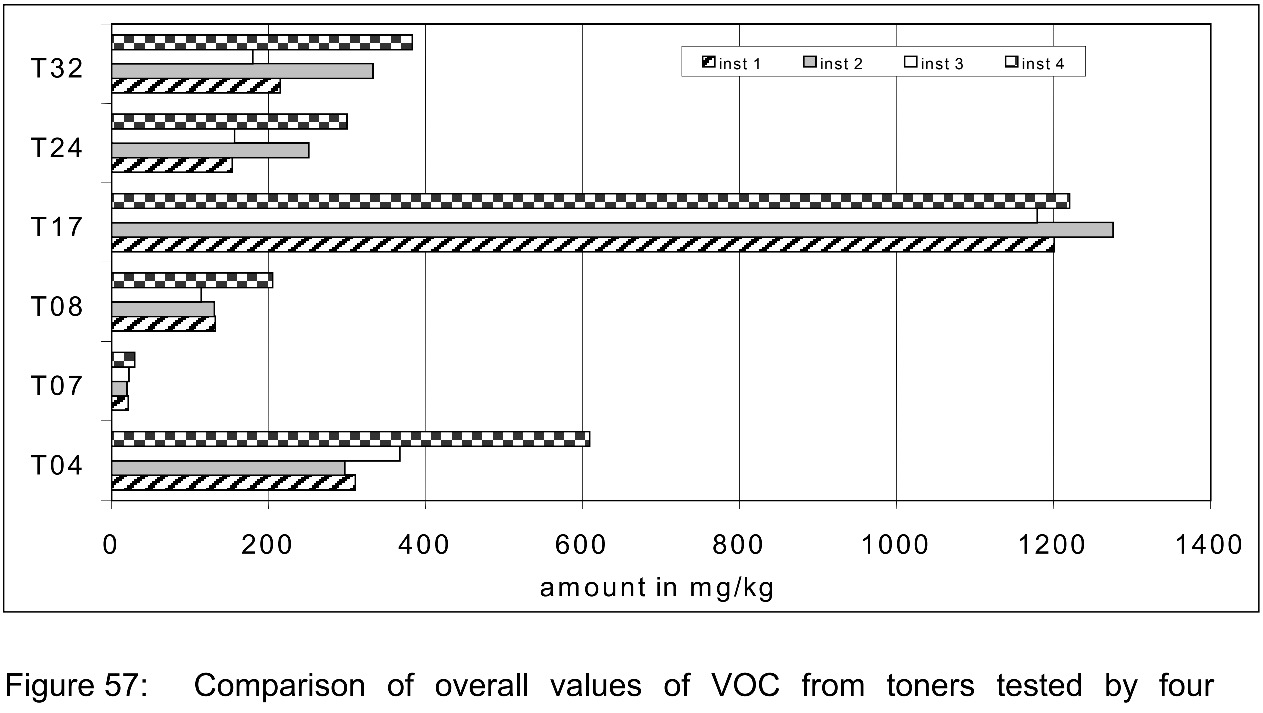


Figure 57: Comparison of overall values of VOC from toners tested by four institutes

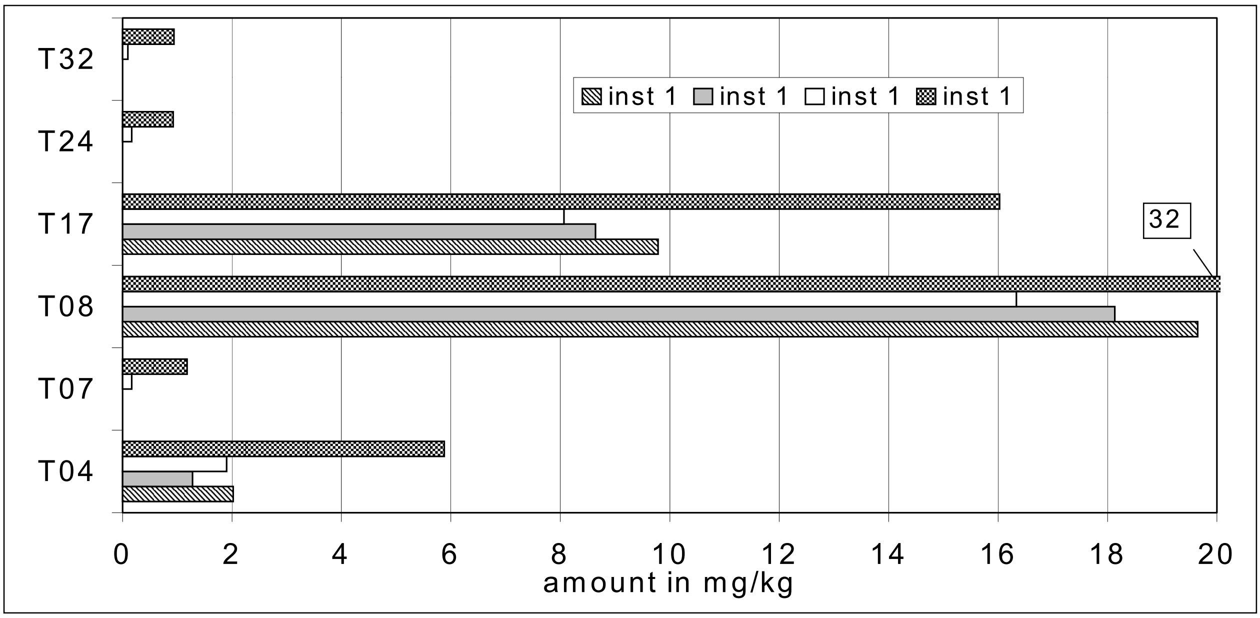


Figure 58: Comparison of benzene values from toners measured by four institutes

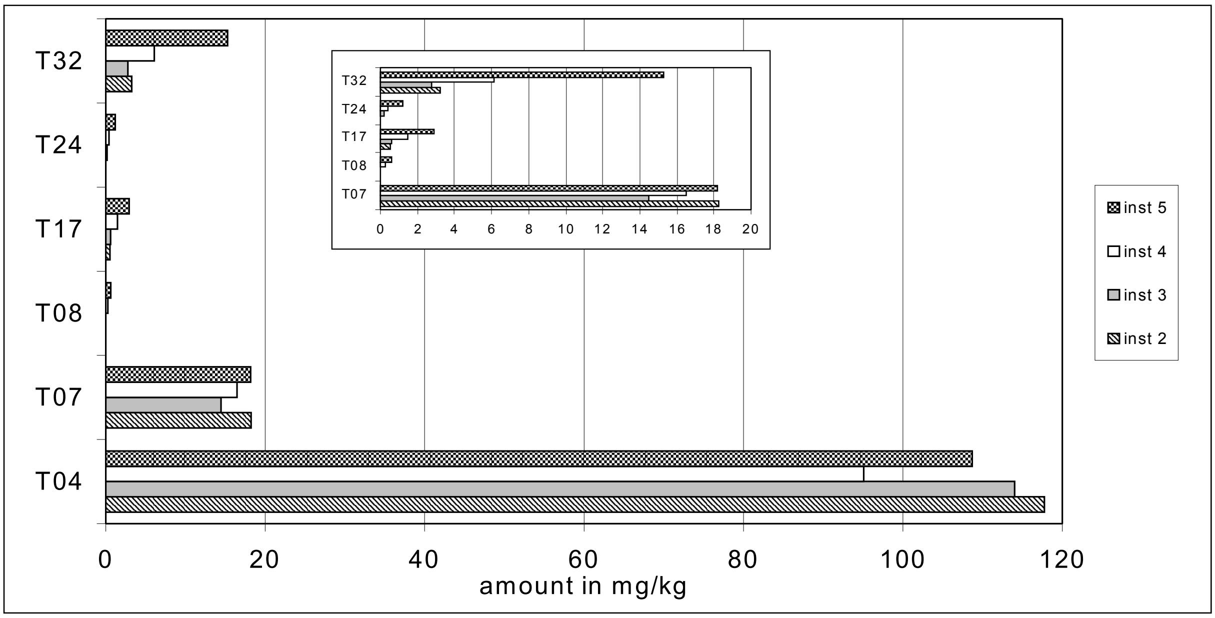


Figure 59: Comparison of styrene values from toners measured by four institutes

8 Discussion and conclusions

Preliminary tests carried out at the beginning of the project made it clear that in principle it is possible to determine dust, ozone and VOC emission rates from hardcopy devices in spite of the short printing times available. First, the so-called ’equilibrium approach’ was favoured [18], for which conditions must be created which lead to an equilibrium concentration in the chamber which remains almost constant over the time (steady state). This can be achieved by either a long enough test duration (2 to 3 hours at an air exchange rate of 1 h^{-1}) or increasing the air exchange rate in the chamber so that equilibrium is achieved within 36 minutes, i.e. the maximum available printing time. This is attainable in principle by air exchange rates of 4 to 5 h^{-1}.

However, common emission test chambers are not equipped for such large air exchange rates, which in particular applies to large chambers, such as the 20m³ chamber used in the project. However it was found for smaller chambers with a volume of 1 m³ that great air exchange rates of 4 - 5 h^{-1} can be achieved, if the chambers are operated either in the rinsing modus or the regular air volume is increased by means other than air flow rate control. The 1m³ chambers mentioned were used because they were specifically developed for VOC emission tests and exhibited an excellent performance due to their clean air supply, low ozone half-lives and outstanding blank value behaviour.

It was also found in the preliminary tests that a relatively high humidity caused considerable problems in the 1m³ chambers during the printing process which led to condensation, even if the temperature was being increased simultaneously in the chamber (Chapter 6.1). The problems were solved by increasing the air exchange rate to 4 – 5 h^{-1} with dry supply air, pre-drying recycled paper and using new paper which released less water during the printing process.

Investigations performed on the hardcopy devices showed that these had very different emission characteristics. Dust emissions determined using gravimetrical methods, illustrated in Figure 60, exhibited rather small differences. Based on available knowledge, they are likely to be mainly the consequence of paper fibres. This statement is based on the one hand on information from members of the project-advisory working group. On the other hand it is experimentally supported by the fact that an increase of the black coverage from 5 % to 20 % failed to result in an increase of the dust emission rate (cf. Section 5.3.1). As the tests showed in addition, dust is also set free by printing empty sheets.

Unlike dust emission, ozone (Figure 61) and VOC emissions (Figure 62) exhibited considerable differences.

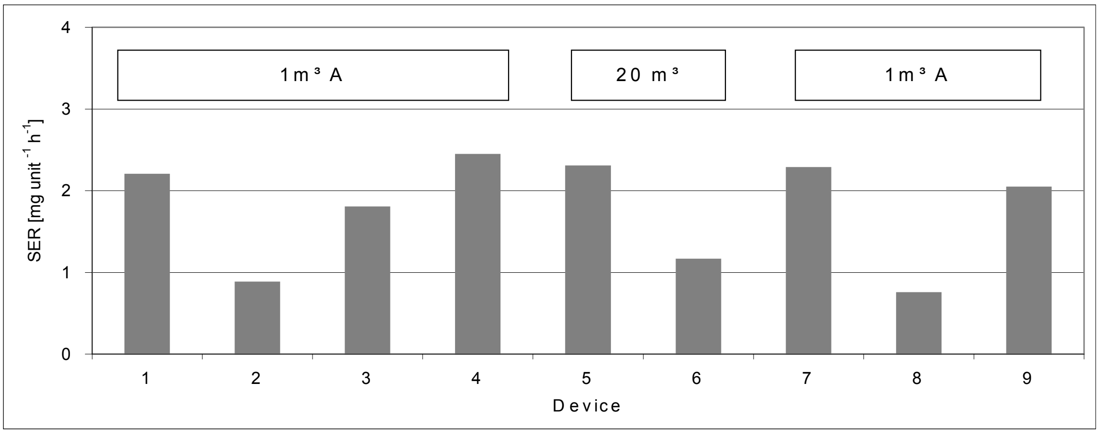


Figure 60: Overview of SER_D determined on recycled paper using gravimetric methods for all devices tested

The additional particle count made it clear that there were devices which exhibited rather small particle emissions while others produced high emissions. A correlation between a gravimetrically determined high dust emission rate and the particle emission rate only partially exists. In order to be able to describe this relationship more precisely further investigation is needed. Because of open questions concerning comparability and evaluation of test results which were obtained in particular using various particle counter methods, these results have not been included in the evaluation of the devices tested. The particle counter method has not been integrated in the developed test method and serves only to provide additional information to the gravimetrically determined dust emission rates.

Figure 61 shows an overview of ozone emission rates for all devices tested under comparable test conditions. Devices 5 and 6 had to be tested, due to their sizes, in the 20m³ test chamber. All other devices were examined in the type A 1m³ chamber. An analysis of ozone emissions showed that there are completely emission-free devices and those with a very low emission, while other devices exhibited considerable ozone emissions.

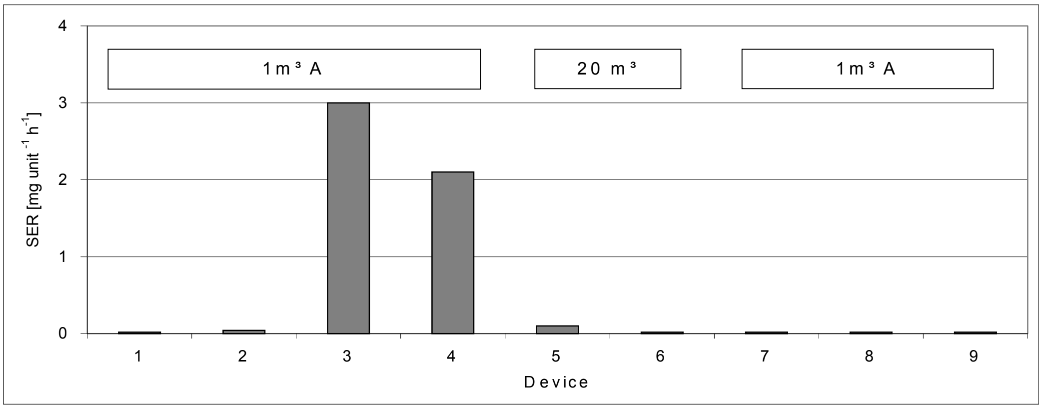


Figure 61: Overview of SER_{ozone} determined on recycled paper for all devices tested

All devices emitted VOCs both in the cold and standby phase and as expected, greater emissions in the printing phase. Marked differences were observed between the various devices.

VOC emissions found were attributed to the toners used and to materials and other consumables used in the devices such as the paper. While the contribution of paper to VOC emissions is rather small, recycled paper in particular showed large SVOC emissions. Based on the present level of knowledge however, the question arises as to what extent SVOC emissions can be reliably measured using the short time measuring procedure used. In the case of ambiguity, calculated emission rates yield smaller values than real ones due to so-called sink effects which include adsorption of semivolatile organic compounds by surfaces (e.g. chamber walls and materials used in the device).

Occurrence of SVOC and an increased water release when using recycled paper, as opposed to new paper, led to the conclusion that new paper has to be used in the testing method for the determination of device emissions on grounds of measurement technology. The reason being that it must be possible to determine emission rates free of any disturbing influence for the purpose of the determination of device emissions, including the related toners. Figure 62 shows an overview of TVOC emission rates for all tested devices determined under comparable test conditions. Devices 5 and 6 had to be measured due to their size in the 20m³ test chamber. All other devices were tested in the type A 1m³ chamber.

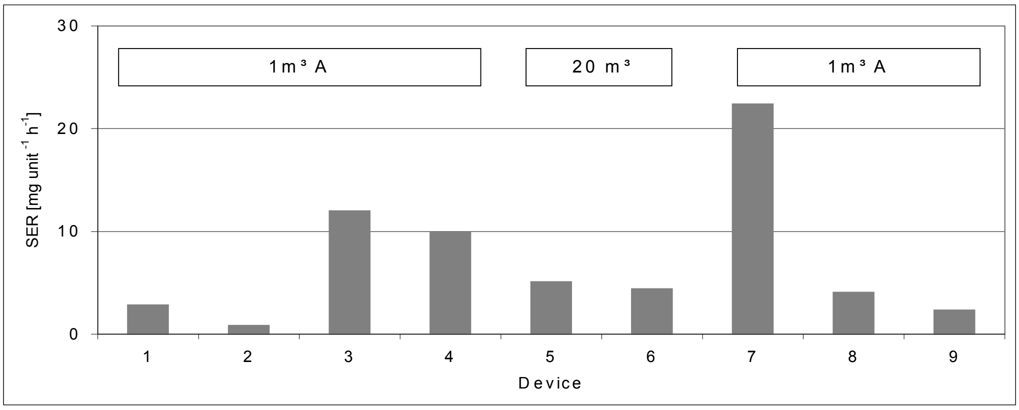


Figure 62: Overview of SER_{TVOC} determined on recycled paper for all devices tested

As far as comparability of different emission test chambers is concerned, this can be considered good but with certain restrictions. Concentrations of emitted substances building up in the air of the 20m³ chambers are clearly smaller than in the 1m³ chambers. The reason being stronger dilution within the larger test chamber volume. In addition, practical air exchange rates do not normally exceed $1h^{-1}$ and the concentrations are still far below the equilibrium concentration within 15 to a maximum 30 minutes. Reduced concentrations principally increase measurement uncertainty.

For these reasons the ’equilibrium approach’ specified above was not applicable to the determination of emission rates from tests in the 20m³ chamber. Instead, VOC emission rates had to be calculated in an integrative way from the beginning of the printing phase to the end of the follow-up phase running over four air exchanges. This means a relatively long time requirement for the tests in large test chambers.

Furthermore the pragmatic conclusion was drawn for the test method (see Chapter 15.8 in the Appendix) that small devices have to be tested in small chambers, and large devices in large chambers. Nevertheless it must be pointed out as the final result that emission rates can be calculated using the test method. This enables the establishment of an evaluation standard which is to a large extent independent of test parameters.

9 Actual room scenario

The issue often arises whether or not data from measurements in emission test chambers may be upscaled to an actual room scenario. Important parameters are test chamber, room size and air exchange rate and on the other hand, emission or concentration values determined by chamber tests in relation to maximum permitted room air concentration values (cf. Section 2.2 Indoor air quality).

A room volume of 17.4 m³ and an air exchange rate of 0.5 h^{-1} is considered as a standard case for the actual room scenario [21]. The investigation of indoor air pollution by VOC from hardcopy devices is focused on TVOCs and styrene and benzene. The TVOC value as an overall parameter is particularly important. Styrene is also a frequent characteristic component in toner emissions and should therefore be tested with utmost care. The same applies to benzene which is a carcinogenic material and its emission must be minimised. Styrene is the only VOC that has been limited by the selection criteria of the environmental label as per RAL-UZ 62 [46], RAL-UZ 85 [50] and RAL-UZ 95 [51].

The maximum proportional concentration target values for the test materials and for dust and ozone are displayed in Table 28. These values were specified so that the target values formulated for indoor air, i.e. 200 to 300 µg m^{-3} for TVOC [36], [37], [61], [62] and 30 µg m^{-3} for styrene may not entirely be taken up by one single product group alone.

The same applies to the limit values specified for the external air (as a comparison): 5 µg m^{-3} for benzene [53], 120 µg m^{-3} for ozone (as an 8hour average) [54] and 40 µg m^{-3} for dust (PM_{10}) [52].

The maximum value of 0.5 µg per m³ for benzene displayed in Table 28 for the contribution of the device corresponds to only a tenth of the benzene concentration permissible in future for external air as per the EU daughter guideline [53] and considers its classification as a carcinogenic compound in particular.

Table 28: Concentration target values for the proportional loading of indoor air by hardcopy devices and derived emission rates and concentration values for chamber tests

Operational modus	**Compound**	**c_R [µg m^{-3}]**	**F**	**SER_{ch} [µg h^{-1}]**	**c_{ch} [µg m^{-3}]**	
					V_{ch}=1m³, n_{ch}=5h^{-1}	V_{ch}=20m³,n_{ch}=1h^{-1}
Printing (1000 sheets, 10 hours), utilization factor 1/10	TVOC	100	0.1	8700	1740	435
	Benzene	0.5		43	8.8	2.2
	Styrene	12		1044	208	52
	Ozone	20		(1740)	(348)	(87)
	Dust	40		3480	696	174
Cold and standby	TVOC$^{1)}$	100	1	870	174	43

$^{1)}$ TVOC for desktop device; 300 µg m^{-3} for freestanding device because larger room and no permanent working place

Some simplifying assumptions have been made in Table 28 to derive permissible emission rates from the concentration target values for the interior (model room). First, sink effects (adsorption by surfaces) are neglected in the model room and the chamber. Secondly it has to be assumed that printers and copiers are not operated continuously over 24 hours and for which they are not designed. For the sake of simplification, a maximum of 1000 sheets is assumed to be printed in ten hours, which is about 10% of the continuous printing capacity of a high-performance desktop device. A utilization factor of 1/10 (0.1) results from this for the printing job. The device is either switched off or on standby phase during the remainder of the day, therefore a utilization factor of 1 is specified. The resulting permissible emission rates (SER_{ch}) can be calculated by Equation 17:

$$\boxed{SER_{ch} = \frac{c_R * n_R * V_R}{F}}$$

Equation 17

The maximum expected concentrations for two different chamber sizes with different air exchange rates are displayed in Table 28 for information. They have been calculated by Equation 18:

$$\boxed{c_{ch} = \frac{c_R * n_R * V_R}{F * n_{ch} * V_{ch}}}$$

Equation 18

c_R:	Concentration of actual analyte in model room	[µg m^{-3}]
c_{ch}:	Concentration of actual analyte in test chamber	[µg m^{-3}]
F:	Utilization factor	[dimensionless]
n_{ch}:	Air exchange rate in test chamber	[h^{-1}]
n_R:	Air exchange rate in model room (0.5 h^{-1})	[h^{-1}]
SER_{ch}:	Emission rate of actual analyte in test chamber	[µg $unit^{-1}h^{-1}$]
V_{ch}:	Volume of test chamber	[m³]
V_R:	Volume of model room (17.4 m³)	[m³]

The emission rates and chamber concentration values for ozone are in brackets in Table 28, as ozone degradation was neglected for the indicated values.

It is evident from Table 28 that much greater concentrations were determined in small emission test chambers such as the 1m³ chamber, which are increasingly used for desktop devices on grounds of measurement technique and costs, than in the larger chamber (20 m³, n = 1 h^{-1}), even if an air exchange rate of up to 5 h^{-1} was used. This is of advantage in view of a reduced measurement uncertainty at greater concentrations, however it may not lead to the assumption that the higher concentrations determined might be critical. The increased concentrations were namely measured because of the test conditions, the device-specific emission rates calculated from the chamber concentration values were identical. This is why permissible emission values for the RAL - UZ criteria are shown in terms of emission rates and not concentration values. The permissible emission rates within the framework of the environmental label as displayed in Table 29 are rounded values which were derived from Table 28 and are indicated in this table in mg h^{-1}.

The higher permissible TVOC emission rate for freestanding devices in the standby phase is obtained from the understanding that these large devices are not used in small offices but usually stand on their own or in large rooms. In addition, some of the freestanding devices exhibited greater emissions in the cold and standby phase than desktop devices did. Therefore the standard area of 17.4 m³ as specified above was not taken as a basis to derive the emission rates, but a standard room with an approximately threefold volume of 50 m³ was considered.

The permissible emission rate for freestanding devices in printing modus however is the same as for desktop devices, since the tested freestanding devices did not show greater emission rates in the printing modus than desktop devices despite sometimes a substantially longer print run.

Table 29: Permissible maxima for emission rates from hardcopy devices as per RAL-UZ 62 new [45], RAL-UZ 85 new [49] and RAL-UZ 114 [48]

Substance	**SER_U [mg h^{-1}]**		
	Printing phase	**Standby phase**	
		Desktop devices	**Freestanding devices**
TVOC	10	1	3
Benzene	0.05	-	-
Styrene	1.0	-	-
Ozone	2	-	-
Dust	4	-	-

10 Summary

The emission behaviour of dust, ozone and VOC (TVOC) of nine hardcopy devices (printers and copiers) were examined within the research project apart from various preliminary tests. It was found that the devices exhibited marked differences in their emission behaviour. This applied in particular to ozone, VOC and TVOC. Dust emissions showed only relatively small differences, predominantly due to the paper. The differences in the ozone emission are based on the different operational principles of the devices used and/or the effectiveness of the ozone filters.

Both the sum (TVOC) and the determined individual VOCs within the VOC emissions showed marked differences. Benzene emission was not found in any of the cases. Styrene and other aromatic compounds, in particular toluene, o-, m- and p-xylene were detected in nearly all devices. The toner used is a possible source of emission for these compounds. However, one of the devices also showed higher toluene emissions for example although the toner used in the device contained only comparatively low toluene contents. Further compounds identified in the devices were benzaldehyde, acetophenone, phenol and hexanal. Paper is to be considered the primary source of hexanal, based on available knowledge. Another device exhibited a surprisingly high proportion of questionable compounds, for which the used toner is a possible cause.

Altogether it has to be concluded that a generally valid statement on the main sources of the determined VOC emissions is not possible on the basis of the available data. Rather, device, toner and paper must be regarded as a system in which in addition to toner and paper, machine materials and further operational materials such as coolants and lubricants are used which may be sources of VOC emission. Machine and operational materials might also be an important cause for the VOC emissions detected in the cold and standby phases for all devices, where large differences were again found between the printers. VOC emissions of the non-switched-on devices and those in the standby modus are not unusual, they are a characteristic of nearly all materials and products [67], [27].

A somewhat different situation resulted for SVOC emissions from almost all devices tested, in particular, when recycled paper was used, especially here in combination with high fixing temperatures of up to 180 °C in the printing phase is to be regarded as a substantial source. It has to be noted however based on current knowledge that SVOC emissions will be not reliably detectable using this test method for hardcopy devices with short duration test procedures.

The "Development of a Test Method for and Investigations into Limiting the Emissions from Printers and Copiers within the Framework of Assigning the Environmental Label" project served as a basis for and its results have been used in this report. Experiences and suggestions of test institutes, manufacturers and the Federal Environmental Agency were considered in three meetings of the project-advisory working group and by further consultation. This testing method has been included into the drafts of the new selection criteria of the environmental label for printers (RAL-UZ 85 [50]), copiers (RAL-UZ 62 [46]) and multi-function devices (RAL-UZ 114 [48]).

Emission test chambers represent the instrumentation basis for the developed test method following ENV 13419-1 [21]. The efficient sampling and analysis procedure as per ISO 16000-6 [38] (Tenax/thermodesorption, GC/MS) has been used for VOC and TVOC measurements from test chamber air. Ozone concentration in the test chamber air is measured using an ozone analyser which works on the principle of chemiluminescence. Dust concentration is determined using a gravimetric procedure under moisture correction. The particle counter procedure used for comparison purposes in a set of tests has not been included into the test provision, since it cannot currently be regarded as a routine test method for dust emissions tests from hardcopy devices.

These definitions essentially conform with the ECMA standard 328 [18]. There are however deviations from the described and so far, frequently practiced procedure for the actual test. On the basis of the generally accepted view that the presence of a person and opening the test chamber during the test for paper supply must be omitted, only a relatively short time is available for uninterrupted printing. Depending on paper supply, paper stack capacity and type of device (printing rate), a maximum of 15 to 30 minutes is feasible for uninterrupted printing by electrophotographic printers and copiers. In order to determine reliable emission rates of the devices on this basis, two different proceedings were established as suitable.

Direct determination of the VOC and ozone emission rate can take place until the end of the printing phase under certain conditions and this applies to the determination of the VOC emission rate until the end of the standby phase.

Another possibility is sampling from the beginning of the printing phase until the end of a directly connected consecutive follow-up phase, which must last for 4 air exchanges. The latter procedure is to be used in each case for the determination of the dust emission rate.

Apart from the determination of emission rates on the tested devices and the development of the test method, a further goal of the project was performing co-operative tests. Four particularly suitable devices were selected out of the nine devices tested for the planned co-operative tests to determine the emission behaviour of hardcopy devices. Only four test institutes participated in this co-operative test from the originally planned five, and only two performed all measurements to the full extent. Comparability of the results between these two institutes was relatively good.

Four institutes participated as planned in the next co-operative tests on the determination of the VOC contents of six different toners. First BAM tested 32 toners and six of those toners which exhibited very clear differences regarding the contained VOC and their concentration in the toner were selected. The result of the co-operative tests was a relatively good comparability among the institutes, although different headspace methods were also used.

Nevertheless it has to be pointed out that content tests on toners permit only very limited forecasts on the emission behaviour of hardcopy devices as a system, since the emissions, as explained above, depend on a number of parameters.

Even if emissions are reproducibly determined under well-defined boundary conditions, these emissions must be evaluated. While emission rates permit a direct comparison of different devices, room air concentrations can also be estimated from them using a number of simplifying hypotheses, e.g. neglecting sink effects. In this instance however it has to be acknowledged that hardcopy devices, both in office and private use, do not print "around the clock" and are not designed to, but print only a fraction of the time due to the recommended monthly printing volumes estimated at a daily 10 %. These concepts were also included in the selection criteria specified above in order to derive permissible emission rates from the target values for interior air for hardcopy devices.

The newly developed test method, which enables a unified and reproducible determination of the emission behaviour of printers, copiers and multi-function devices has established an important step to reducing the material emissions into indoor air together with the selection criteria for the environmental label.

For electro photographic colour devices and ink jet printers, which have not been subject to investigation in this project, the test method is in principle transferable but should first be used experimentally. These experiences and issues of limitation of further individual VOCs, except benzene and styrene, and a determination (and characterisation) of dust emissions using other procedures such as particle counter procedures, should be considered in a possible later revision of the test method and the selection criteria for the environmental label. In particular the unidentifiable compounds detected in some devices and toners require closer attention in the future. Methods of reducing VOC and SVOC contents of recycled papers should also be considered, since these may represent a substantial source of emission in the use in hardcopy devices.

11 References

[1] Ad-hoc-Arbeitsgruppe aus Mitgliedern der Innenraumlufthygiene-Kommission (IRK) des Umweltbundesamtes und des Ausschusses für Umwelthygiene der AGLMB. Richtwerte für die Innenraumluft: Basisschema. (Guideline values for indoor air: basic scheme.) Bundesgesundheitsblatt 39 (1996) pp 422-425.

[2] Ad-hoc-Arbeitsgruppe aus Mitgliedern der Innenraumlufthygiene-Kommission (IRK) des Umweltbundesamtes und des Ausschusses für Umwelthygiene der AGLMB. Richtwerte für die Innenraumluft: Pentachlorphenol. (Guideline values for indoor air: pentachlorophenol.) Bundesgesundheitsblatt 40 (1997) pp 234-236.

[3] Black M. S., Worthan A. W. 1999. Emissions from office equipment. Proceedings of the 8th International Conference on Indoor Air Quality and Climate - Indoor Air ’99, Vol 2, pp 454-459. Edinburgh.

[4] c’ t: Anrüchig - Wie gesundheitsschädlich sind Laserdrucker? (How health damaging laser printers are?) c’t 17 (2001) pp 26

[5] Computerbild: Test - Gift im Toner. (Test: poison in toners.) Computerbild 8 (2002), pp 180 - 188

[6] Deutsches Institut für Bautechnik (German Institute for Building Tecnology), DIBt-Mitteilungen 32 (2001) 1, pp 3-12

[7] Diabate S., Völkel K., Wottrich R.: Krank durch Nanopartikel. (Sick through nanoparticles.) NACHRICHTEN - Forschungszentrum Karlsruhe 34 (2002) pp 75 - 83

[8] DIN 19309 Papier für Kopierzwecke (Paper for copying)

[9] DIN 33870, Ausgabe: 2001-01 Informationstechnik - Büro- und Datentechnik - Anforderungen und Prüfungen für die Aufbereitung von gebrauchten Tonermodulen schwarz für elektrophotographische Drucker, Kopierer und Fernkopierer (Information technology. Office and data technology. Requirements and tests on the processing of used black toner modules for electro photographic printers, copiers and remote copiers)

[10] DIN EN 12281, Ausgabe: 2003-01 Druck- und Büropapier - Anforderungen an Kopierpapier für Vervielfältigungen mit Trockentoner; Deutsche Fassung EN 12281:2002 (Printing and office paper. Requirements on copying paper for multiplication using dry toners. German edition)

[11] DIN EN 20287, Edition: 1994-09 Papier und Pappe - Bestimmung des Feuchtegehaltes - Wärmeschrankverfahren (Paper and cardboard - Water content determination – Drying oven method) (ISO 287:1985); Deutsche Fassung (German Edition) EN 20287: 1994

[12] DIN EN ISO 14024, Edition: 2001-02 Umweltkennzeichnungen und -deklarationen - Umweltkennzeichnung Typ I - Grundsätze und Verfahren (ISO 14024:1999); (Environmental labels and declarations – Environmental labels Type I – Fundamentals and procedures. German Edition) Deutsche Fassung EN ISO 14024:2000

[13] DIN V ENV 717-1, (Pre-norm) Edition: 1999-02 Holzwerkstoffe - Bestimmung der Formaldehydabgabe - Teil 1: Formaldehydabgabe nach der Prüfkammer-Methode (Wooden materials – Determination of formaldehyde emission – Part 1: Formaldehyde emission as per test chamber method); German Edition ENV 717-1: 1998

[14] ECA-Report No. 18, Evaluation of VOC Emissions from Building Products - Solid Flooring Materials. EUR 17334 EN, 1997.

[15] ECA-Report No. 19, Total Volatile Organic Compounds (TVOC) in Indoor Air Quality Investigations. EUR 17675 EN, 1997.

[16] ECA-Report No. 2, Formaldehyde Emission from Wood Based Materials: Guideline for the determination of steady state concentrations in test chambers. EUR 12196 EN, April 1989

[17] ECA-Report No. 8, Guideline for the Characterization of Volatile Organic Compounds (VOC) emitted from Indoor Materials and Products using Small Test Chambers"

[18] ECMA-Standard 328, Detection and measurement of chemical emissions from electronic equipment, August 2001 (www.ecma.ch).

[19] Englert, N.: Richtwerte für die Innenraumluft: Kohlenmonoxid. (Guideline values for indoor air: carbon monoxide.) Bundesgesundheitsblatt 40 (1997) pp 425-428.

[20] Englert, N.: Richtwerte für die Innenraumluft: Stickstoffdioxid. (Guideline values for indoor air: nitrogen dioxide.) Bundesgesundheitsblatt 41 (1998) pp 9-12.

[21] European pre-standard ENV 13419-1: Bauprodukte - Bestimmung der Emission von flüchtigen organischen Verbindungen - Teil 1: Emissionsprüfkammer-Verfahren (Building products – Determination of emission of volatile organic compounds – Part 1: Emission test chamber method), October 1999.

[22] European pre-standard ENV 13419-2: Bauprodukte - Bestimmung der Emission von flüchtigen organischen Verbindungen - Teil 2: Emissionsprüfzellen-Verfahren (Building products – Determination of the emission of volatile organic compounds – Part 2: Emission test cell method), October 1999.

[23] European pre-standard ENV 13419-3: Bauprodukte - Bestimmung der Emission von flüchtigen organischen Verbindungen - Teil 3: Verfahren zur Probenahme, Lagerung der Proben und Vorbereitung der Prüfstücke (Building products – Determination of emission of volatile organic compounds – Part 3: Method for sampling, storing and preparing samples), October, 1999.

[24] Heinrich U.: Ultrafeine Partikeln. In Symposium „Grenzwerte für chemische Einwirkungen an Arbeitsplätzen“. (Ultrafine particles. Symposium “Limiting values for chemical impacts in the working place“.) BIA - Report 4 / 98. Ed.: Hauptverband der gewerblichen Berufsgenossenschaften - HVBG, Sankt Augustin (1998), pp 163 – 174

[25] International pre-standard ISO / CD 16000-6: Indoor air and emission test chamber air- determination of VOCs; active sampling on TENAX TA, Thermal desorption and gas chromatography, November 2000.

[26] ISO 554, Edition: 1976-07 Normalklimate für die Konditionierung und / oder Prüfung; Anforderungen (Standard climates for conditioning and/or testing. Requirements)

[27] Jann, O., Wilke, O,. Brödner, D.: Entwicklung eines Prüfverfahrens zur Ermittlung der Emission flüchtiger organischer Verbindungen aus beschichteten Holzwerkstoffen und Möbeln. (Development of a test method for the determination of emissions of volatile organic compounds from laminated wooden materials and furniture.) UBA-Texte 74/99, UBA, Berlin, 1999

[28] Jann, O., Wilke, O,. Walther, W., Ullrich, D.: Entwicklung eines standardisierbaren Prüfverfahrens zur Bestimmung des Eintrages von Holzschutzmittel-Wirkstoffen aus behandeltem Holz, Altholz und daraus hergestellten Holzwerkstoffen in die Luft. (Development of a standardisable test method for the determination of emissions of wood protecting agents into the air from treated wood, used wood and wooden materials made from it.) UBA-Projekt-Nr. 126 06 003, Bundesanstalt für Materialforschung und -prüfung (BAM), Abschlußbericht, Berlin, 1997. UBA-Texte 51/99, Umweltbundesamt, Berlin, 1999.

[29] Jann, O., Wilke, O.: Möglichkeiten und Grenzen bei der Bestimmung von SVOC-Emissionen aus Materialien und Produkten. (Possibilities and limits for determination of SVOC emissions from materials and products.) VDI-Bericht Nr. 1656, 2002, pp 357-367.

[30] Jann, O.: Vergleichende Untersuchungen über die Formaldehydemission von Holzwerkstoffen in Prüfkammern. Teil 1 und 2. (Comparative tests on formaldehyde emissions of wooden materials in test chambers. Part 1 and 2.) Research report 106 04 122, UBA-FB 96-034 UBA-Texte 23/96, Umweltbundesamt, Berlin, 1996

[31] Kommission Innenraumlufthygiene (IRK) (Commission Indoor Air Hygiene), Stand 2002, http://www.umweltbundesamt.de/uba-info-daten/daten/irk.htm#4]]

[32] Konzeption der Bundesregierung zur Verbesserung der Luftqualität in Innenräumen. (Concept of the Federal Government to improve indoor air quality.) Bundesumweltministerium, September 1992, Bonn.

[33] LGA (Dr. Jungnickel) personal communication, February 2002

[34] Link, B.: Richtwerte für die Innenraumluft: Quecksilber. (Guideline values for indoor air: mercury.) Bundesgesundheitsblatt 42 (1999) pp 168-174.

[35] Meyer, U., Möhle, K., Eyerer, P. et al.: Entwicklung, Bau und Inbetriebnahme einer 1 m³-Bauteilmesskammer zur Bestimmung von Emissionen aus Endprodukten. (Development, construction and commissioning of a 1m³ test chamber for building components for the determination of emissions from end products.) Staub - Reinhaltung der Luft 54, 1994: pp 137 - 142.

[36] Mølhave, L., Clausen, G.: The use of TVOC as an indicator in IAQ investigations, Proceedings of Indoor Air 1996, Vol. 2, pp 37-46.

[37] Mølhave, L.: Volatile Organic Compounds, Indoor Air Quality and Health. Indoor Air, 4 (1991): pp 357-376

[38] Normentwurf DIN ISO 16000-6: Bestimmung von VOC in der Innenraumluft und in Prüfkammern, Probenahme auf TENAX TA, thermische Desorption und Gaschromatographie (Determination of VOC in indoor air and in test chambers, sampling of TENAX TA, thermodesorption and gas chromatography) / MSD and FID, September 2002.

[39] ÖKO-TEST: Außen hui, innen pfui. (Outside ok, inside yuk.) ÖKO-TEST 8 (2001), pp 26 - 29

[40] ÖKO-TEST: Verstaubte Technik. (Dusty technique.) ÖKO-TEST 2 (2002), pp 30 - 32

[41] Plehn, W., Marutzky, R., Salthammer, T.: Einflüsse auf das Wohnklima. In: Informationsdienst Holz - Wohngesundheit im Holzbau. (Influences on living space climate. In: Information services timber – indoor health in timber structures.) Editor: Deutsche Gesellschaft für Holzforschung (German Wood Research Association) München and Forstabsatzfond, Bonn, März 1998.

[42] RAL - UZ 102 für emissionsarme Wandfarben. (Low-emission wall paints.) Edition: May 2000 Deutsches Institut für Gütesicherung und Kennzeichnung e.V., Siegburger Straße 39, 53757 Sankt Augustin, www.blauer-engel.de

[43] RAL - UZ 12 a für schadstoffarme Lacke. (Low-emission varnishes.) Edition: January 1997 Deutsches Institut für Gütesicherung und Kennzeichnung e.V., Siegburger Straße 39, 53757 Sankt Augustin, www.blauer-engel.de

[44] RAL - UZ 38 für emissionsarme Produkte aus Holz und Holzwerkstoffen. (Low-emission products from wood and wooden materials). Edition: April 2002 Deutsches Institut für Gütesicherung und Kennzeichnung e.V., Siegburger Straße 39, 53757 Sankt Augustin, www.blauer-engel.de

[45] RAL - UZ 62 für Kopiergeräte NEU. (Copiers NEW.) Edition: probably 2003 Deutsches Institut für Gütesicherung und Kennzeichnung e.V., Siegburger Straße 39, 53757 Sankt Augustin, www.blauer-engel.de

[46] RAL - UZ 62 für Kopiergeräte. (Copiers) Edition: January 2002 Deutsches Institut für Gütesicherung und Kennzeichnung e.V., Siegburger Straße 39, 53757 Sankt Augustin, www.blauer-engel.de

[47] RAL - UZ 76 für emissionsarme Holzwerkstoffplatten. (Low-emission wood boards.) Edition: June 2001 Deutsches Institut für Gütesicherung und Kennzeichnung e.V., Siegburger Straße 39, 53757 Sankt Augustin, www.blauer-engel.de

[48] RAL - UZ 114 für Hardcopygeräte, (Hardcopy devices) Deutsches Institut für Gütesicherung und Kennzeichnung e.V., Siegburger Straße 39, 53757 Sankt Augustin, www.blauer-engel.de

[49] RAL-UZ 85 für Drucker NEU. (Printers NEW.) Edition: 2003 Deutsches Institut für Gütesicherung und Kennzeichnung e.V., Siegburger Straße 39, 53757 Sankt Augustin, www.blauer-engel.de

[50] RAL-UZ 85 für Drucker. (Printers) Edition: March 2002 Deutsches Institut für Gütesicherung und Kennzeichnung e.V., Siegburger Straße 39, 53757 Sankt Augustin, www.blauer-engel.de

[51] RAL-UZ 95 Faxgeräte, Fernkopierer und Faxkombinationsgeräte (Fax machines, remote copiers and fax combination devices.) Edition: October 2002 Deutsches Institut für Gütesicherung und Kennzeichnung e.V., Siegburger Straße 39, 53757 Sankt Augustin, www.blauer-engel.de

[52] Richtlinie 1999/30/EG des Rates vom 22. April 1999 über Grenzwerte für Schwefeldioxid, Stickstoffdioxid und Stickstoffoxide, Partikel und Blei in der Luft (Guideline 1999/30/EG of the Committee of 22. April 1999 on limiting values for sulphur dioxide, nitrogen dioxide and nitrogen oxide, particles and lead in the air), ABl. No. L 163 of 29.6. 1999, pp 41 (1. Daughter guideline)

[53] Richtlinie 2000/69/EG des Europäischen Parlaments und des Rates vom 16. November 2000 über Grenzwerte für Benzol und Kohlenmonoxid in der Luft, (Guideline 2000/69/EG of the European Parliament and Committee of 16. November 2000 on limiting values for benzene and carbon monoxide in the air) ABl. No. L 313 of 13.12.2000, pp 12; ber. ABl. No. L 111 of 20.4.2001, pp 31 (2. Daughter guideline)

[54] Richtlinie 2002/3/EG des Europäischen Parlaments und des Rates vom 12. Februar 2002 über den Ozongehalt der Luft (Guideline 2002/3/EG of the European Parliament and Committee of 12. February 2002 on ozone content in the air), ABl. No. L 67 of 9.3.2002, pp 14 (3. Daughter guideline)

[55] Riediger G., Möhlmann C.: Ultrafeine Aerosole an Arbeitsplätzen. (Ultrafine aerosols in the working place.) Gefahrstoffe - Reinhaltung der Luft 61 (2001) pp 429 – 434

[56] Riediger G.: Ultrafeine Aerosole an industriellen Arbeitsplätzen. (Ultrafine aerosols in industrial working places.) Gefahrstoffe - Reinhaltung der Luft 63 (2003) pp 65

[57] Sagunski, H., Heinzow B.: Richtwerte für die Innenraumluft: Bicyclische Terpene (Leitsubstanz α-Pinene). (Guideline values for indoor air: bicyclic terpenes – guiding substance: α-pinenes) Bundesgesundheitsblatt - Gesundheitsforschung - Gesundheitsschutz 4 (2003) pp 346 - 352.

[58] Sagunski, H., Roßkamp E.: Richtwerte für die Innenraumluft: Tris(2-chlorethyl)phosphat. (Guideline values for indoor air: tris(2-chloroethyl) phosphate) Bundesgesundheitsblatt - Gesundheitsforschung - Gesundheitsschutz 3 (2002) pp 300 - 306.

[59] Sagunski, H.: Richtwerte für die Innenraumluft: Styrol. (Guideline values for indoor air: styrene) Bundesgesundheitsblatt 41 (1998) pp 392-421.

[60] Sagunski, H.: Richtwerte für die Innenraumluft: Toluol. (Guideline values for indoor air: toluene) Bundesgesundheitsblatt 39 (1996) pp 416-421.

[61] Seifert, B.: Regulating Indoor Air, Proceedings of the 5th International Conference on Indoor Air Quality and Climate - Indoor Air ´90: 35 - 49.

[62] Seifert, B.: Richtwerte für die Innenraumluft (Guideline values for indoor air), Bundesgesundheitsblatt 1999, 42, 270-278.

[63] Smola T., Georg H., Hohensee H.: Gesundheitsgefahren durch Laserdrucker? (Health risks through laser printers?) Gefahrstoffe - Reinhaltung der Luft 62 (2002), 295 – 301

[64] Stone V., Donaldson K.: Small particles - big problem. Aerosol Soc. Newsletter 33 (1998), pp 12 – 14

[65] Test: Laserdrucker (Laser printers). 7 (1999) 72 – 77

[66] Wensing M, Kummer T., Riemann A., Schwampe W. 2002. Emissions from electronic devices: examination of computer monitors and laser printers in a 1m³ emission test chamber. Proceedings of the 9th International Conference on Indoor Air Quality and Climate - Indoor Air ’02, Vol 2 pp 554-559. Monterey: Indoor Air ’02.

[67] Wilke O., Jann O.: Untersuchung und Ermittlung emissionsarmer Klebstoffe und Bodenbeläge (Investigating and identifying low-emission adhesives and floor coverings). UBA - Texte 27 / 03, UBA (2003)

[68] Witten, J., H. Sagunski und B. Wildeboer: Richtwerte für die Innenraumluft: Dichlormethan (Guideline values for indoor air: dichloromethane). Bundesgesundheitsblatt 40 (1997) pp 278-284.

12 List of abbreviations

AgBB	Committee for Health-related Evaluation of Building Products (Ausschuss für die gesundheitliche Bewertung von Bauprodukten)
CEN	European Standardisation Committee
COST	European Committee in the Field of Scientific and Technical Research
DIBt	German Institute of Building Technology (Deutsches Institut für Bautechnik)
DKD	German Calibration Services (Deutscher Kalibrierdienst)
DcL	Detection limit (Nachweisgrenze)
DrL	Determination limit (Bestimmungsgrenze)
ECA	European Collaborative Action
ECMA	European Computer Manufacturer Association
FID	Flame ionisation detector
GC	Gaschromatography
LCI	Lowest Concentration of Interest
LGA	State Trade Institute, Nuremberg (Landesgewerbeanstalt, Nürnberg)
HS	Headspace
IRK	Commission Indoor Air Hygiene (=Kommission Innenraumlufthygiene)
MS	Mass spectrometer
NIK	Lowest Concentration of Interest (=niedrigste interessierende Konzentration)
POM	Particulate Organic Matter
RAL	German Institute for Quality Assurance and Labelling (Deutsches Institut für Gütesicherung und Kennzeichnung e.V.)
RV	Co-operative test (Rundversuch)
SVA	Expert committee (Sachverständigenausschuss)
SVOC	Semi Volatile Organic Compound
TC	Technical Committee
TDS	Thermodesorption
TVOC	Total Volatile Organic Compounds
UBA	Federal Environmental Agency (Umweltbundesamt)
UZ	Environmental Label (Umweltzeichen)
VOCEM	Interlaboratory Comparison for Measuring VOC Emissions
VOC	Volatile Organic Compound
VVOC	Very Volatile Organic Compound
WG	Working group

13 List of figures

14 List of tables

15 Appendix

15.1 Overview of all test results for ozone, dust and TVOC

Table 30 Overview of all test results for ozone, dust and TVOC

Device	No.	Test conditions						Dust					Ozone			TVOC		
		Test date	Ch V [m³]	n [h^{-1}]	t_{Pr} [min]	t_T [min]	n_{sheet} [unit]	m_{St} [µg]	V [m³]	c_D [mg m^{-3}]	SER_U [mg $u^{-1}h^{-1}$]	SER_u [kP $u^{-1}h^{-1}$]	H'[c] [min]	c_{max} [µg m^{-3}]	SER_u [mg $u^{-1}h^{-1}$]	t [h]	c_{TVOC} [µg m^{-3}]	SER_u [mg $u^{-1}h^{-1}$]
1	1 / 1	26.02.02	1	4.0	20	50	364[d]	152.5	0.7	0.22	2.20	11.6	7.5	< 0.002	< 0.02	0.303	494	2.83
	1 / 2	27.02.02[a]	1	4.0	27	57	500	103.3	0.8	0.12	1.01	25.2	4.0	< 0.002	< 0.02	0.350	338	1.79
	1 / 3	28.02.02	1	4.0	21	57	366[d]	39.2	0.7	0.06	0.65	2.40	4.0	< 0.002	< 0.02	0.297	380	2.19
	1 / 4	04.03.02	1	4.0	25	57	478[d]	111.8	0.7	0.15	1.37	5.57	4.0	< 0.002	< 0.02	0.342	631	3.39
	1 / 5	05.03.02[b]	1	4.0	27	57	499	61.8	0.8	0.08	0.68	9.44	4.5	< 0.002	< 0.02	0.350	1956	10.38
	1 / 6	06.03.02	1	4.0	27	57	499	38.4	0.8	0.05	0.42	4.20	3.0	< 0.002	< 0.02	0.358	725	3.81
	1 / 7	07.03.02	1	4.0	27	57	499	46.5	0.8	0.06	0.51	2.46	3.0	< 0.002	< 0.02	0.358	735	3.86
	1 / 8	17.04.02	1	4.0	24	54	443[e]	111.8	1.1	0.10	0.90	3.69	1.7	< 0.002	< 0.02	0.32	66	0.41
2	2 / 1	11.03.02	1	4.0	36	66	500	105.1	0.9	0.12	0.88	0.81	3.5	3.2	0.04	0.494	190	0.86
3	3 / 1	12.03.02	1	4.0	22	52	500	126.9	0.7	0.19	1.80	3.23	1.5	106.8	3.0	0.296	2105	12.0
	3 / 2	23.04.02	1	4.0	19	49	500	153.0	0.8	0.20	2.06	3.00	1.7	94.9	2.4	0.288	1522	8.9
	3 / 3	18.06.02	1	4.0	21	51	500	108.2	0.7	0.16	1.60	2.34	1.9	132.4	3.0	0.288	1836	10.7
	3 / 4	20.06.02	1	4.4	20	50	500	179.8	0.7	0.25	2.70	2.96	1.1	120.5	4.6	0.288	1730	10.6
	3 / 5	24.09.02	1	4.7	10	10	250	ND	ND	ND	ND	ND	2.2	156.1	3.0	n. b	n. b	ND
	3 / 6	24.09.02	1	4.7	20	20	250	ND	ND	ND	ND	ND	2.4	150.2	2.6	n. b	n. b	ND
	3 / 7	24.09.02	1	4.7	10	10	250	ND	ND	ND	ND	ND	2.5	173.9	2.9	n. b	n. b	ND
	3 / 8	24.09.02	1	4.7	13	13	250	ND	ND	ND	ND	ND	2.7	179.8	2.8	n. b	n. b	ND
	3 / 9	05.12.02	1	4.7	10	70	250	25.4	2.5	0.01	0.33	2.65	2.7	127.8	2.6	0.132	673	6.80
	3 / 10	05.12.02	1	4.7	20	90	500	34.1	3.4	0.01	0.21	3.98	1.8	166.0	2.8	0.383	406	2.30
	3 / 11	12.12.02	20	1.0	10	250	250	91.8	9.2	0.01	5.00	0.18	5.0	14.6	2.5	4.20	22	11.2

Device	No.	Test conditions						Dust					Ozone			TVOC		
		Test date	Ch V [m³]	n [h^{-1}]	t_{Pr} [min]	t_T [min]	n_{sheet} [unit]	m_{St} [µg]	V [m³]	c_D [mg m^{-3}]	SER_U [mg $u^{-1}h^{-1}$]	SER_u [kP $u^{-1}h^{-1}$]	H'^c [min]	c_{max} [µg m^{-3}]	SER_u [mg $u^{-1}h^{-1}$]	t [h]	c_{TVOC} [µg m^{-3}]	SER_u [mg $u^{-1}h^{-1}$]
4	4 / 1	14.03.02	1	4.0	31	61	500	228.2	0.7	0.31	2.44	1.23	2.1	102.8	2.1	0.461	2095	9.87
	4 / 2	24.04.02	1	4.0	30	60	500	72.2	0.8	0.09	0.72	0.05	2.3	130.4	2.4	0.461	1439	6.80
	4 / 3	13.06.02	1	4.0	26	56	500	31.2	0.8	0.04	0.34	0.20	1.9	144.3	3.3	0.422	576	2.80
	4 / 4	02.07.02	1	4.4	15	45	235[d]	5.8	0.6	0.01	0.13	1.15	2.4	162.0	2.8	n. b	n. b	ND
	4 / 5	03.07.02	1	4.4	32	62	500	8.1	0.8	0.01	0.10	2.09	1.9	177.8	3.9	0.461	334	1.72
	4 / 6	11.07.02	20	1.0	32	62	500	112.1	0.9	0.13	5.04	0.09	11.2	38.7	2.9	0.422	47	2.71
5	5 / 1	19.03.02	20	1.0	24	54	500	36.6	0.7	0.05	2.30	2.87	11.5	1.6	0.1	0.338	72	5.10
6	6 / 1	21.03.02	20	1.0	32	62	1901[d]	25.1	0.8	0.03	1.16	4.39	8.0	< 0.002	< 0.02	0.437	84	4.41
	6 / 2	25.04.02	20	1.0	37	67	2500	56.2	1.1	0.05	1.81	8.86	7.0	< 0.002	< 0.02	0.542	70	3.35
7	7 / 1	10.04.02	1	4.0	17	47	99	46.2	0.6	0.08	0.88	2.22	4.0	< 0.002	< 0.02	0.208	2850	20.1
	7 / 2	11.04.02	1	4.0	15	45	89[d]	119.1	0.6	0.19	2.28	1.43	4.0	< 0.002	< 0.02	0.208	3215	22.4
8	8 / 1	18.04.02	1	4.0	28	58	500	73.1	0.8	0.09	0.75	28.7	1.7	< 0.002	< 0.02	0.350	764	4.07
	8 / 2	12.06.02	1	4.0	28	58	500	91.13	0.7	0.13	1.08	67.3	1.9	< 0.002	< 0.02	0.375	421	2.15
	8 / 3	25.06.02	1	4.4	28	58	500	131.5	0.8	0.16	1.46	37.6	1.8	< 0.002	< 0.02	0.375	255	1.39
	8 / 4	09.07.02	20	1.0	28	58	500	79.0	0.8	0.10	4.14	0.10	6.5	< 0.002	< 0.02	0.367	24	1.56
9	9 / 1	04.07.02	1	4.4	27	57	500	163.9	0.7	0.22	2.04	16.1	ND	< 0.002	< 0.02	0.389	438	2.34
	9 / 2	02.12.02	1	4.4	13	73	250	111.5	2.8	0.04	0.99	20.7	ND	< 0.002	< 0.02	0.163	209	1.84
	9 / 3	03.12.02	1	4.4	27	87	500	127.9	3.2	0.04	0.57	16.9	1.8	< 0.002	< 0.02	0.413	359	1.97
	9 / 4	10.12.02	20	1.0	14	267	250	183.6	9.2	0.02	7.63	1.61	6.5	< 0.002	< 0.02	4.20	39	2.33

Overview of symbols and abbreviations used in Table 30

$Ch\ V$:	Volume of test chamber used	[m³]
t_{Pr}:	Printing time	[min]
t_T:	Total sampling time	[min]
t:	Average printing time	[h]
n_{sheet}:	Number of sheets printed	[piece]
C_D	Dust concentration determined by gravimetric method	[mg m^{-3}]
C_{TVOC}:	TVOC concentration determined by analysis	[µg m^{-3}]
H':	Ozone half-life	[min^{-1}]
n:	Air exchange rate	[h^{-1}]
SER_u:	Emission rate for the actual substance	[mg u^{-1} h^{-1}]
c_{max}:	Maximum ozone concentration	[µg m^{-3}]

gray: Tests on various new white sheets of paper
a: Zero per cent of black coverage, i. e. printing empty sheets
b: 20 % of black coverage
c: Determined in loaded state
d: Printing prematurely terminated due to technical failure
e: New start after technical failure
ND: non detected
f: kP stands for kilo (1000) particles

15.2 Selected climate curves

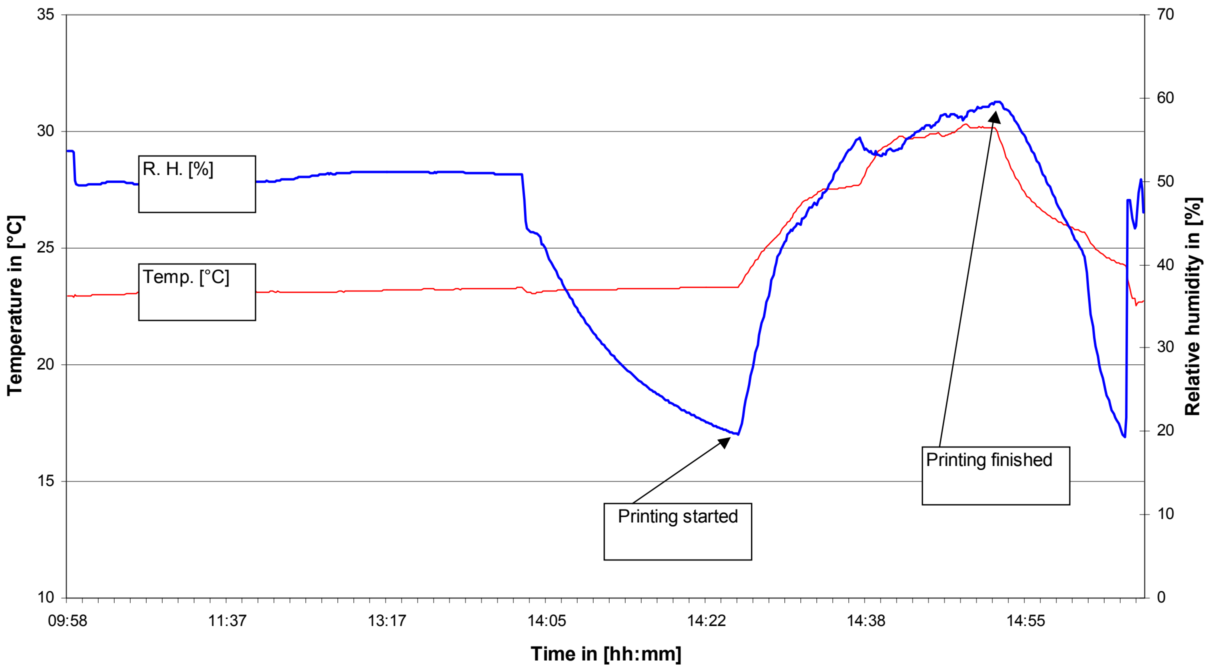


Figure 63: Climate curve during printing phase for device 1 (Test: 27.2.02), type A 1m³ chamber

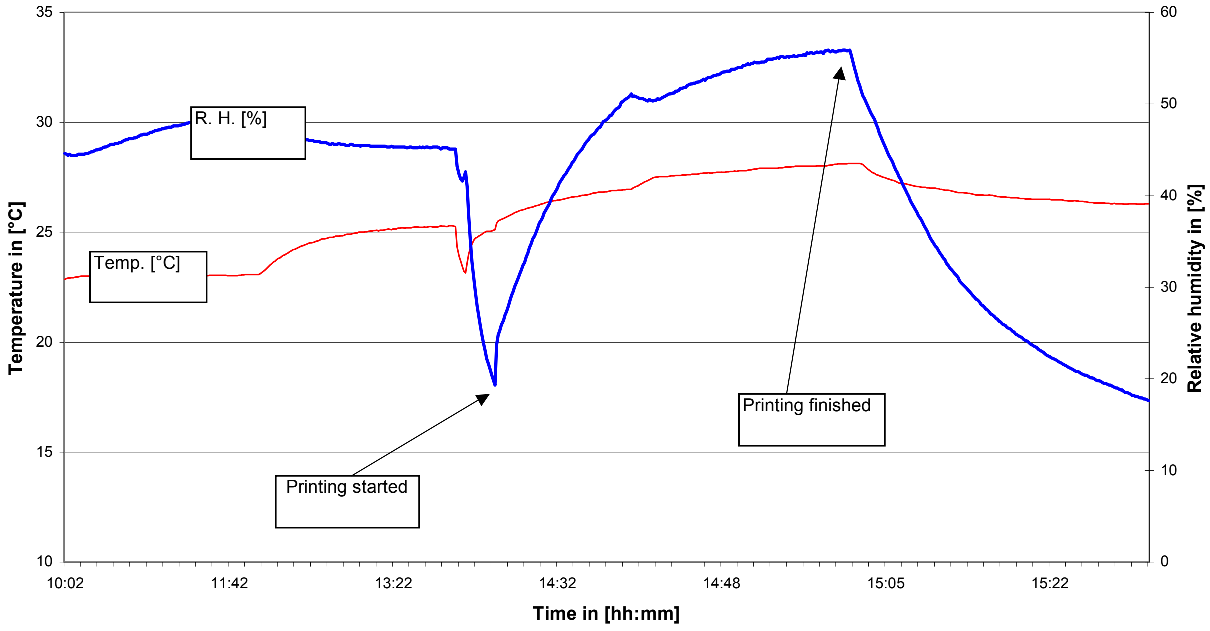


Figure 64: Climate curve during printing phase for device 2 (Test: 11.3.02), type A 1m³ chamber

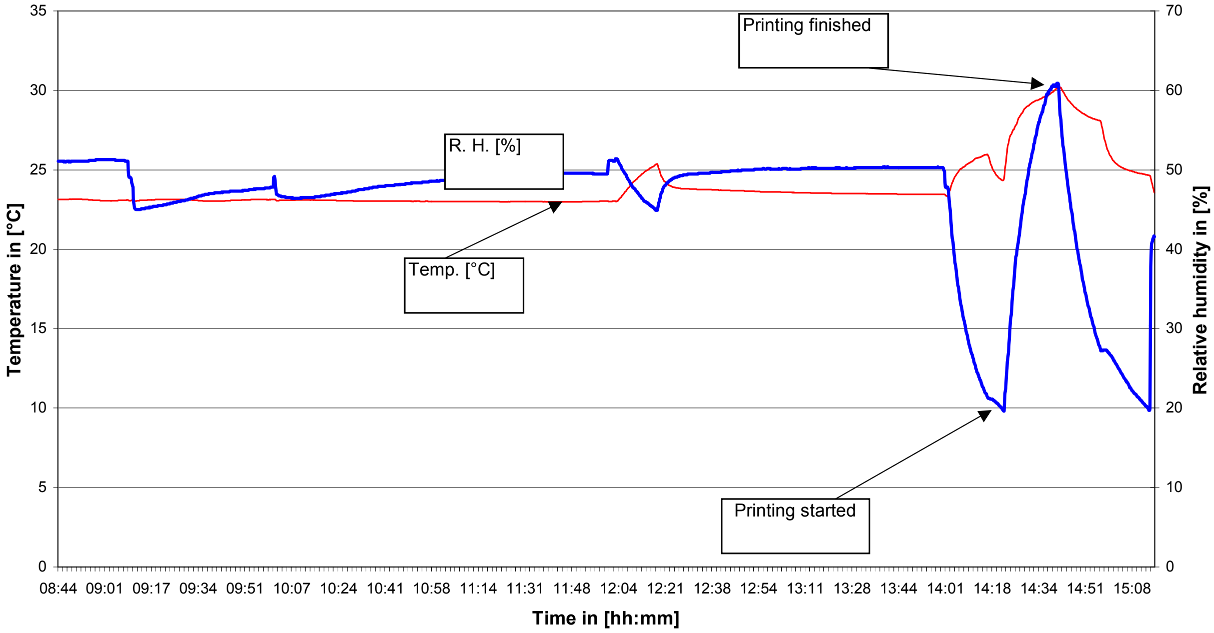


Figure 65: Climate curve during printing phase for device 3 (Test: 12.3.02), type A 1m³ chamber

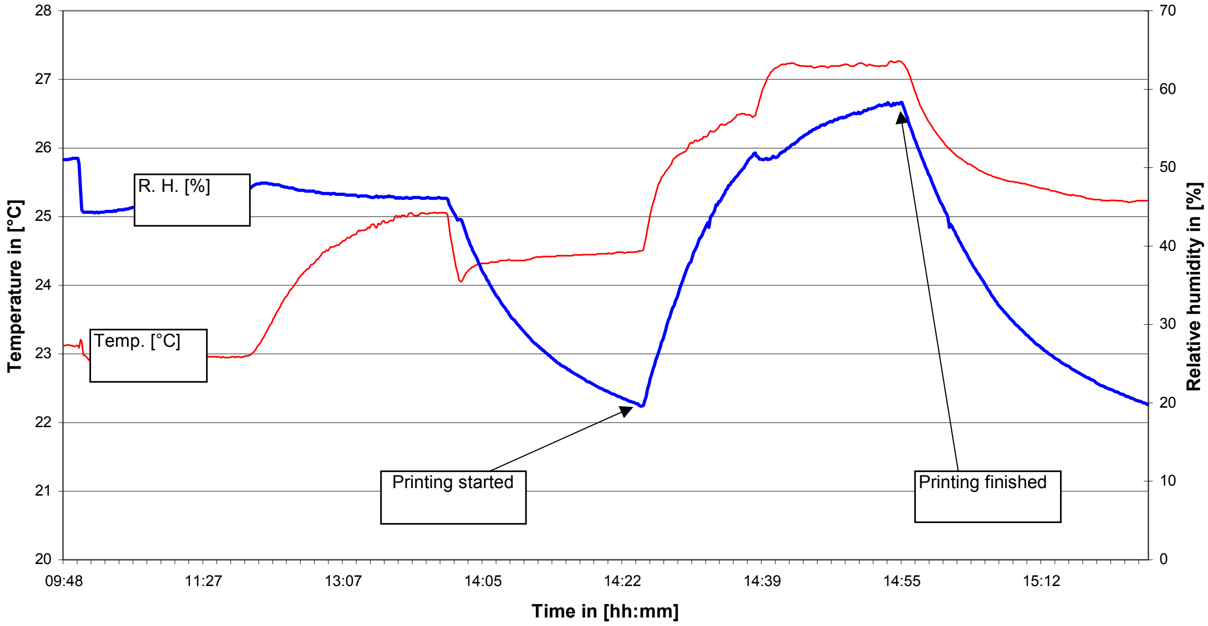


Figure 66: Climate curve during printing phase for device 4 (Test: 14.3.02), type A 1m³ chamber

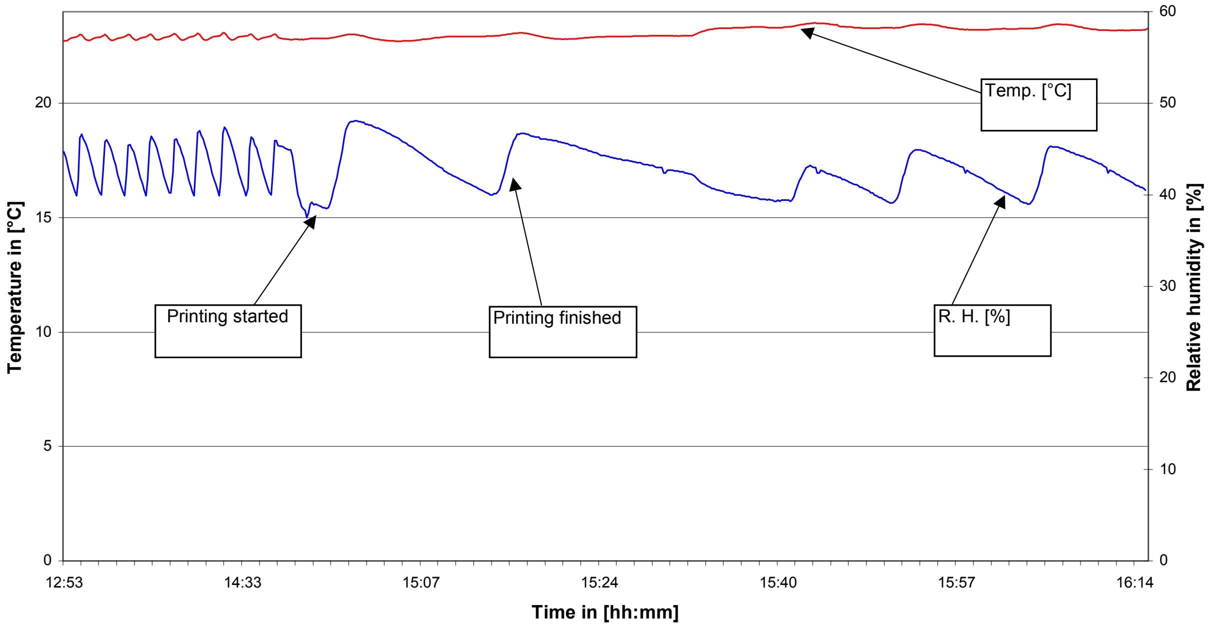


Figure 67: Climate curve during printing phase for device 5 (Test: 19.3.02), 20m³ chamber

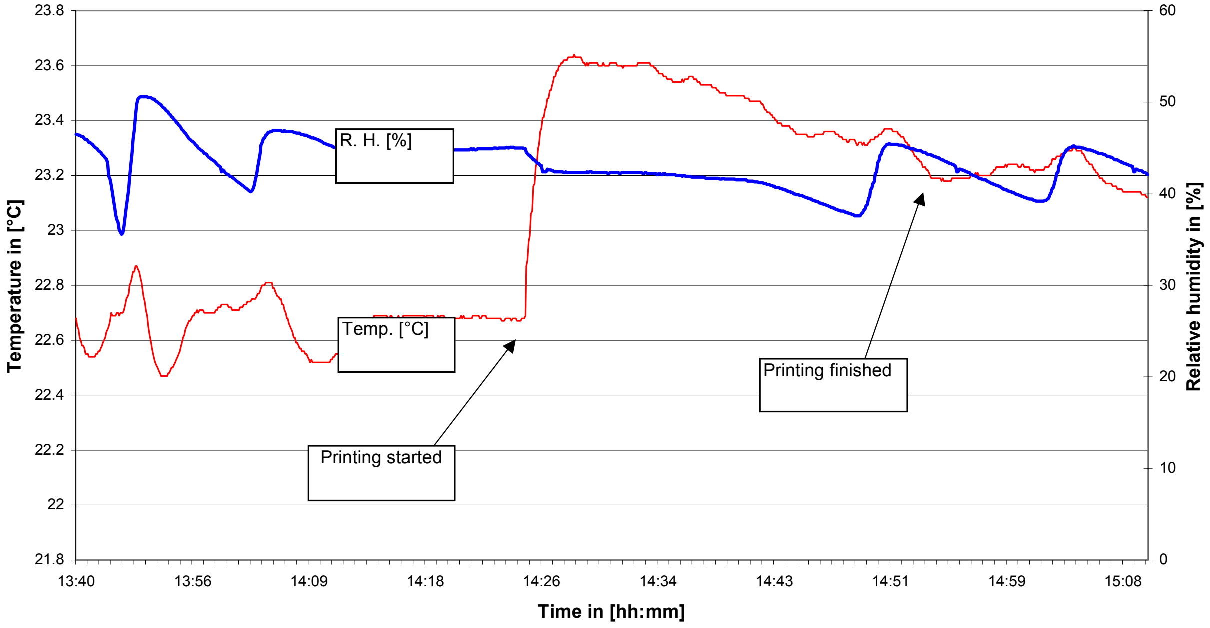


Figure 68: Climate curve during printing phase for device 6 (Test: 21.3.02), 20m³ chamber

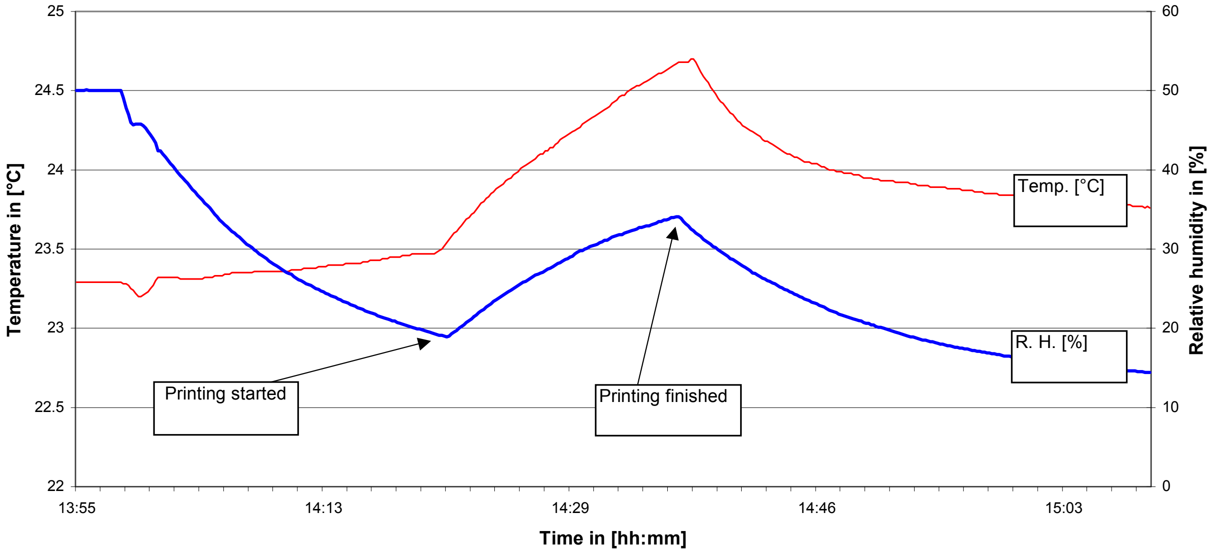


Figure 69: Climate curve during printing phase for device 7 (Test: 10.04.02), type A 1m³ chamber

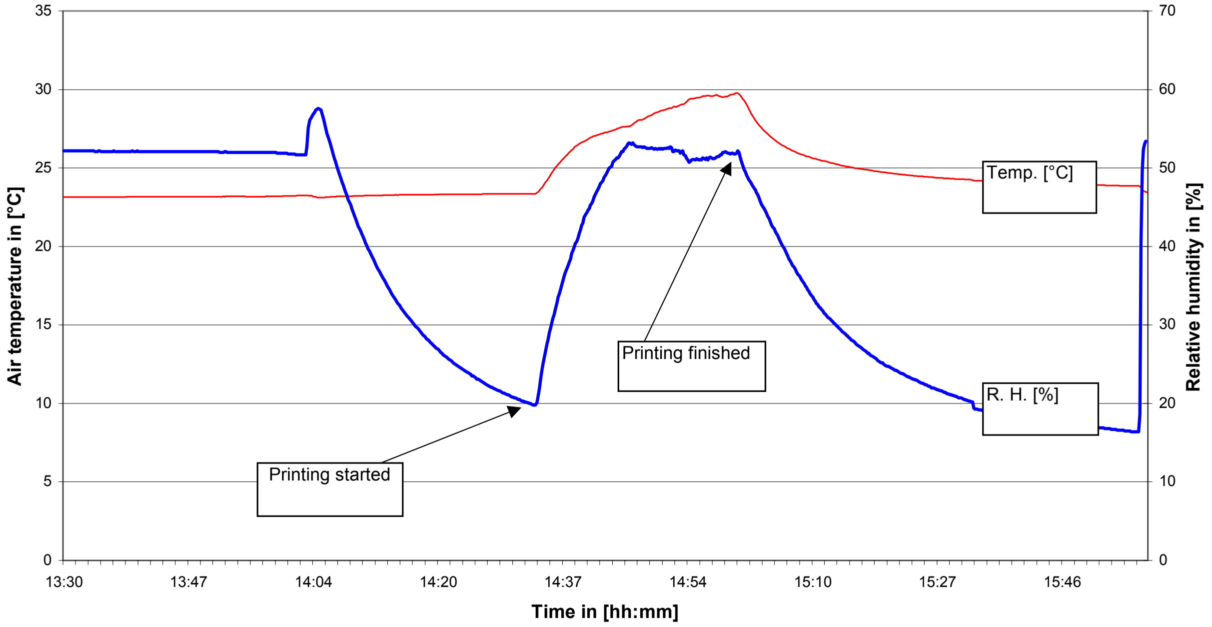


Figure 70: Climatic parameters during the printing phase for device 8 (Test: 18.04.02), type A 1m³ chamber

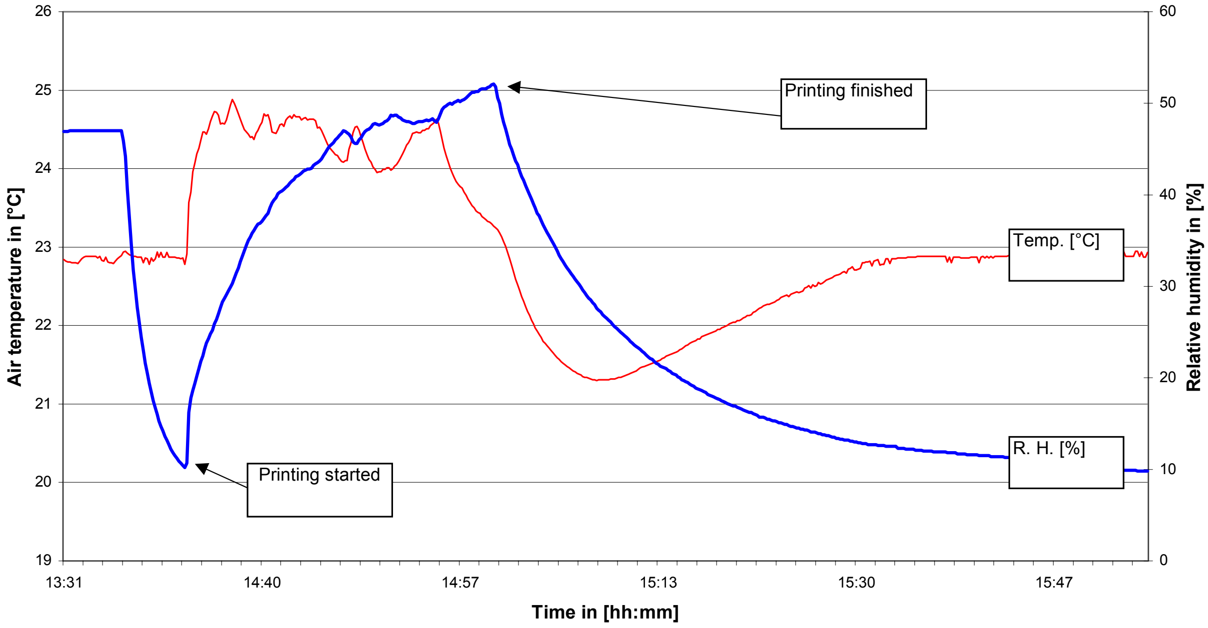


Figure 71: Climate curve during printing phase for device 9 (Test: 18.04.02)

15.3 Ozone curves

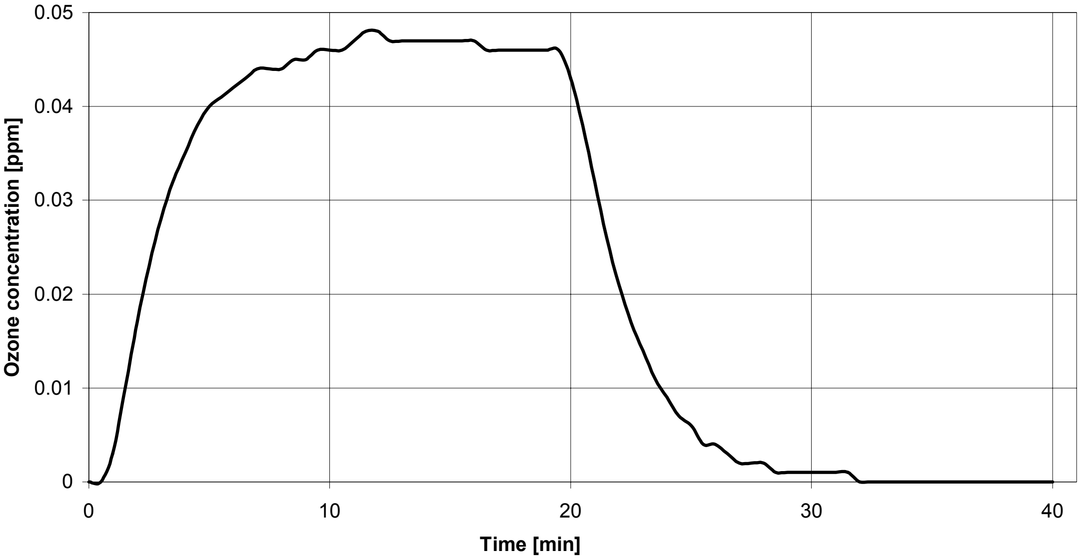


Figure 72: Ozone curve during printing phase for device 3 (Test: 12.3.02), type A 1m³ chamber

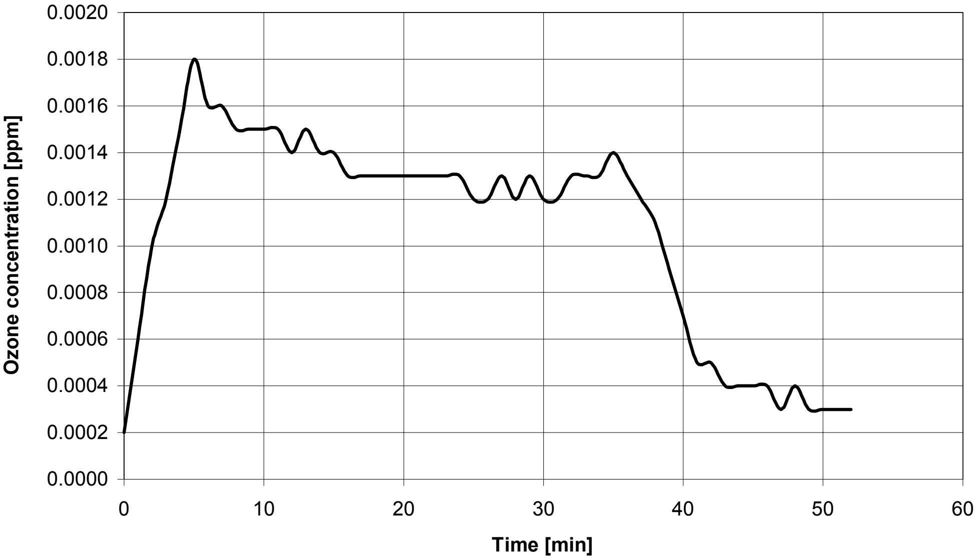


Figure 73: Ozone curve during printing phase for device 4 (Test: 14.3.02), type A 1m³ chamber

15.4 Grey scale linearisation pattern for the 5 % print

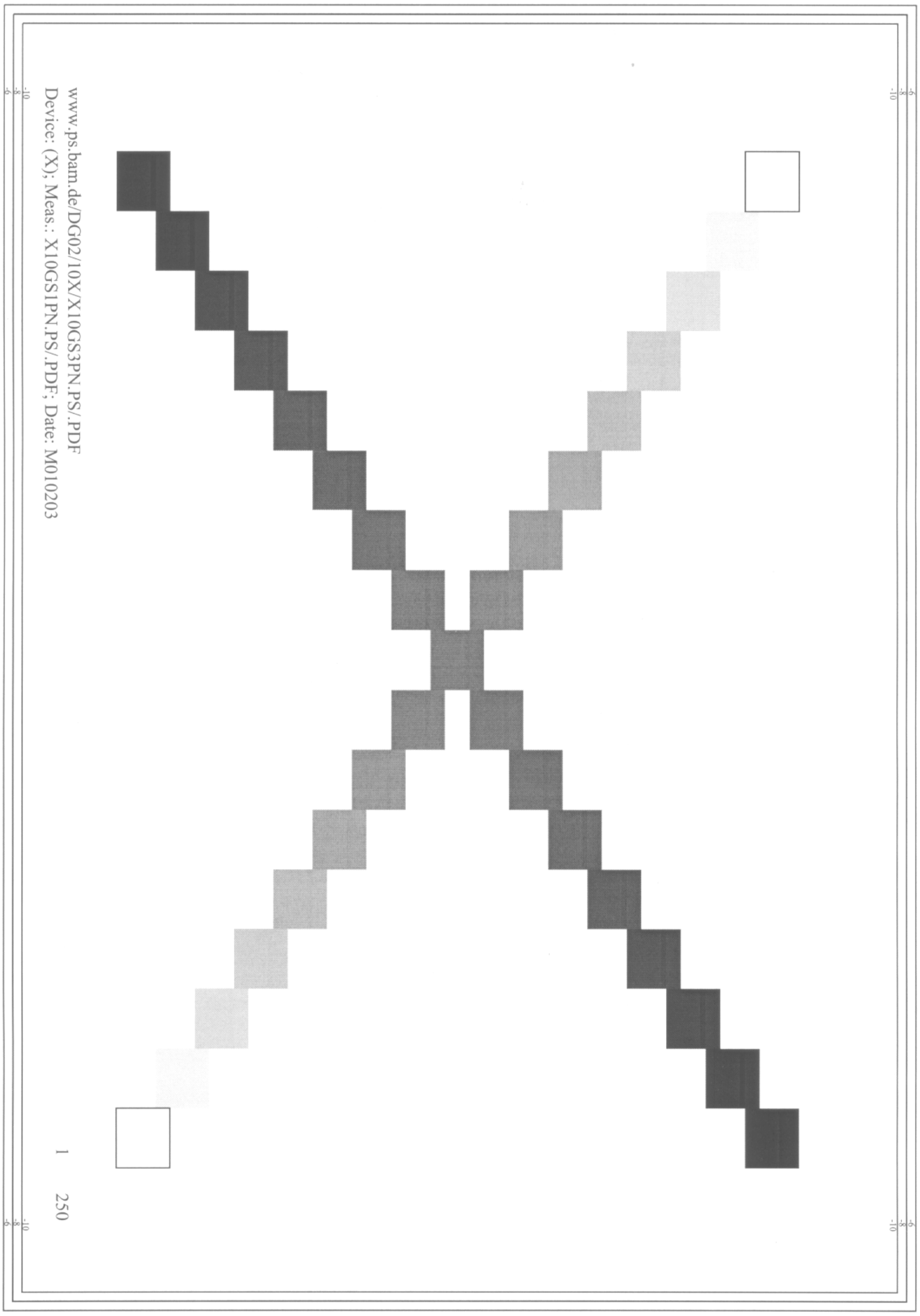


Figure 74: Grey scale linearisation pattern for the 5 % print

15.5 Printer pattern 5% black coverage

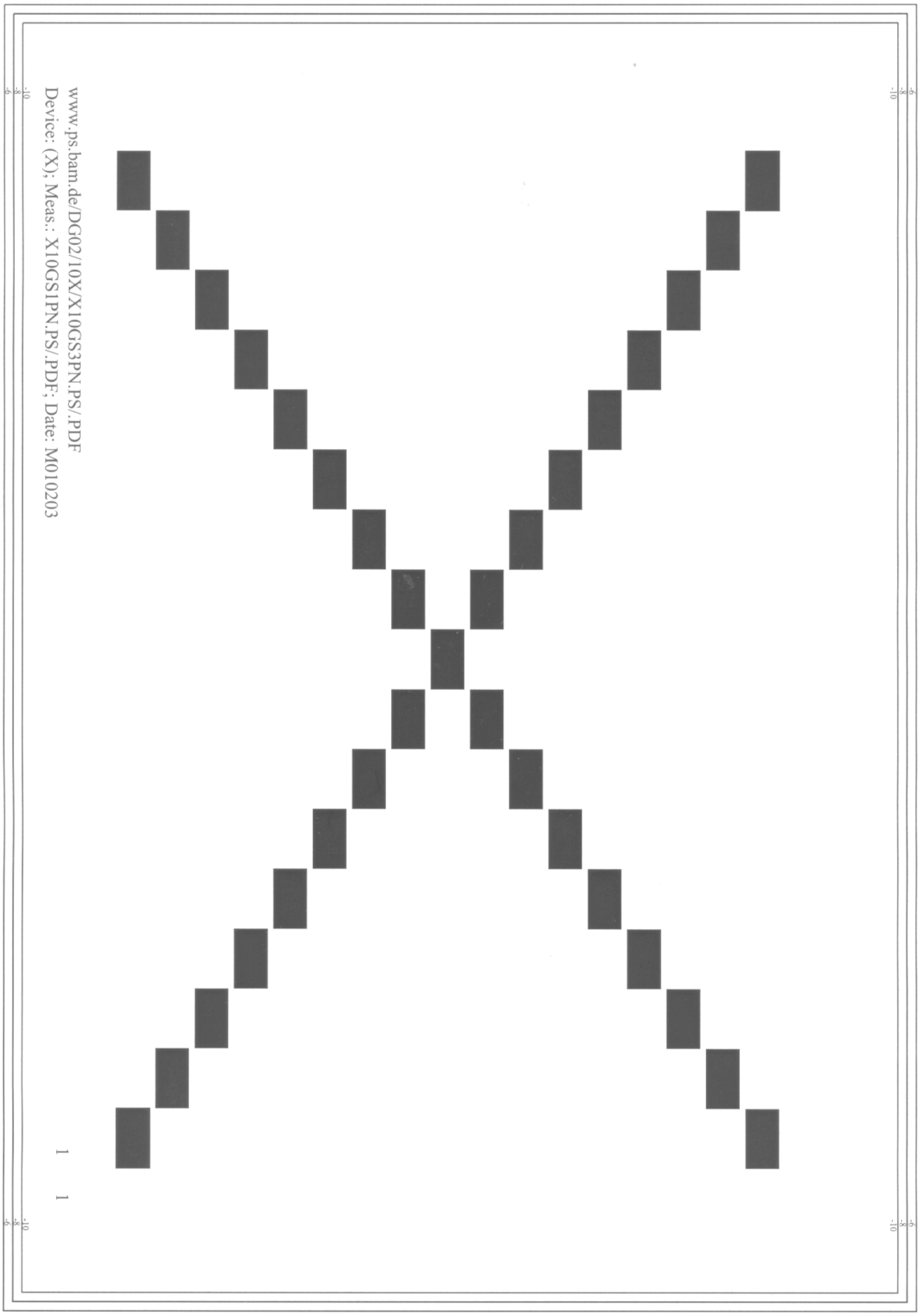


Figure 75: Printer pattern 5% black coverage, per DIN 33870 [9]

15.6 Figures of the analysis devices used

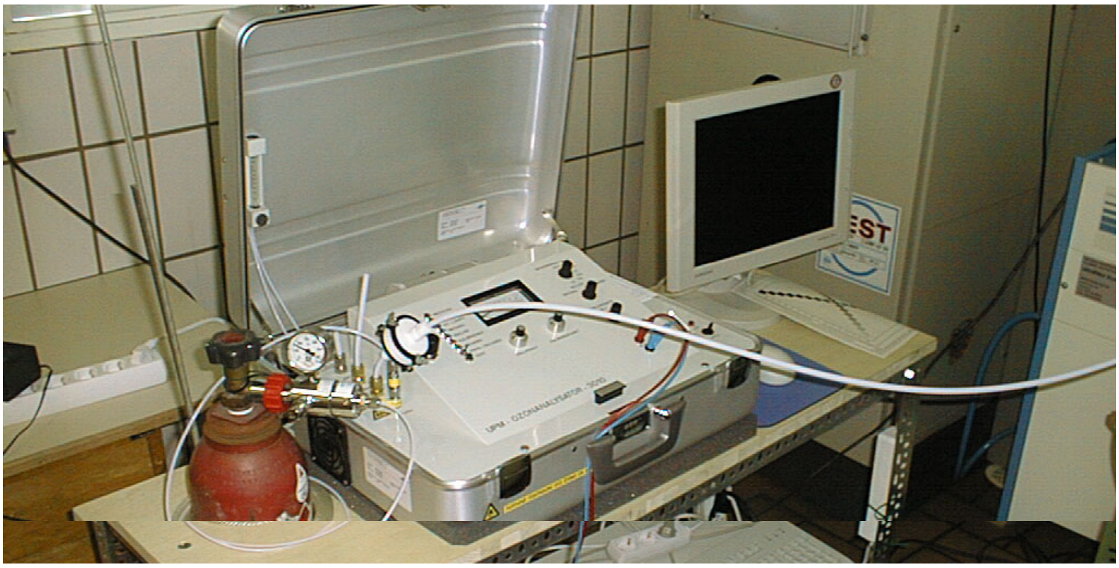


Figure 76: Ozone analyser

Figure 77: Particle counter

Figure 78: Ultra microscale

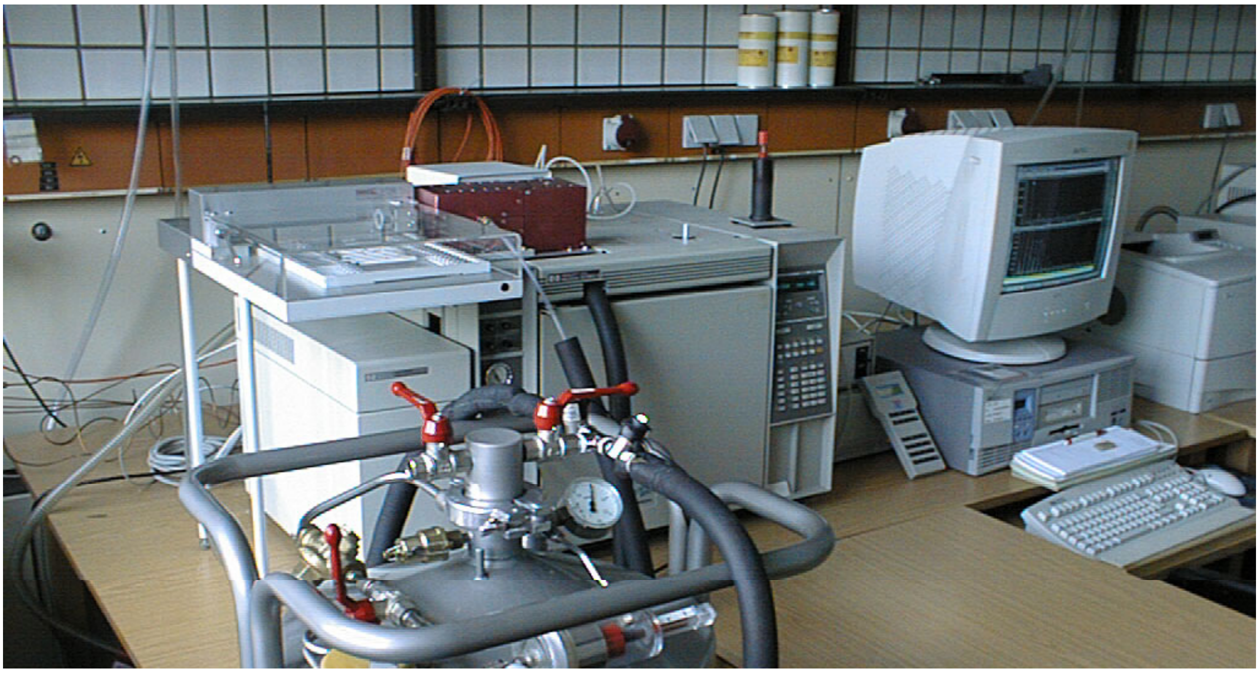


Figure 79: Gaschromatograph with an MS detector

15.7 Members of the project-advisory working group

A project-advisory working group was formed to provide advice while carrying out the project. The working group held three meetings in which preliminary results were presented and discussed and advice was given during the project.

The members of the working group, which convened in a small or large circle depending on the topic, belonged predominantly to research and/or testing institutes, equipment manufacturers and the Federal Environmental Agency (UBA). The names of all members of this advisory board are listed below.

The aim of the activity of the working group was to integrate the experts' opinion and knowledge into the selection criteria and the associated testing method at an as early stage as possible, since reasonable results and practicable requirements can only be achieved in consent with those involved. The activities mentioned did form a basis for the official RAL hearing procedure for the revised RAL UZ 62 and RAL UZ 85 environmental labels and the new ZU 114 environmental label, but did not pre-empt the RAL procedure.

The helpful guidance to the project provided by the members of the advisory panel is once again gratefully acknowledged.

Table 31: Members of the project-advisory working group of the first meeting on 18. February 2002

Ms. Böttcher - Tiedemann Federal Environmental Agency (UBA)	Mr. Pesch Canon Deutschland GmbH
Mr. Bake UBA	Mr. Rockstroh BAM
Mr. Bazlen HEWLETT-PACKARD CO.	Mr. Schneider BAM
Mr. Heimann Berufsgenossenschaftliches Institut für Arbeitsschutz (BIA)	Mr. Ullrich UBA
Ms. Jacobs Federal Environmental Agency (UBA), Berlin	Mr. van Heiningen Oce - Technologies
Mr. Jann BAM	Mr. Wensing TÜV Nord mbH
Mr. Jungnickel (LGA)	Mr. Wilke BAM
Mr. Lengnink Ricoh Deutschland GmbH	Mr. Zietlow Sony International (Europe) GmbH
Mr. Noske BAM	

Table 32: Members of the project-advisory working group of the second meeting on 17. July 2002

Mr. Bazlen HEWLETT-PACKARD CO.	Mr. Lengnink Ricoh Deutschland GmbH
Mr. Bake UBA	Mr. Noske BAM
Ms. Brödner BAM	Mr. Pesch Canon Deutschland GmbH
Mr. Englert UBA	Mr. Rockstroh BAM
Mr. Georg BIA	Mr. Seibel RW TÜV
Mr. Govers Oce	Mr. Schneider BAM
Mr. Heimann BIA	Mr. van Heiningen Oce - Technologies
Mr. Herb Kyocera - Mita	Mr. Wensing TÜV Nord mbH
Mr. Hofacker Sharp	Ms. Wiedebusch UBA
Mr. Horn BAM	Mr. Wild Xerox Deutschland GmbH
Ms. Jacobs UBA	Mr. Wilke BAM
Mr. Jann BAM	Mr. Zietlow Sony International (Europe) GmbH
Mr. Jungnickel LGA	

Table 33: Members of the project-advisory working group of the third meeting on 31. January 2003

Ms. Böttcher - Tiedemann UBA	Mr. Noske BAM
Mr. Bake UBA	Mr. Rockstroh BAM
Ms. Brödner BAM	Mr. Schneider BAM
Mr. Horn BAM	Mr. Ullrich UBA
Ms. Jacobs UBA	Mr. van Heiningen Oce - Technologies
Mr. Jann BAM	Mr. von der Heyden BIA
Mr. Jungnickel LGA	Mr. Wensing WKI Braunschweig
Mr. Kleine BIA	Mr. Wilke BAM
Ms. Kubina LGA	

June 2003

Test method

for the determination

of emissions from hardcopy devices

with respect to awarding the environmental label

for office devices RAL-UZ 62, RAL-UZ 85 and RAL-UZ 114

Contents

Preface

This test method was developed to implement new emission criteria (VOC, ozone and dust) in the requirements RAL-UZ 62, RAL-85 and 114 for awarding the environmental label for hard copy devices (printers, photocopiers and multifunction devices). In particular it is based on the ECMA 328 standard detailed in ECMA (European Computer Manufacturers Association) and the DIN ENV 13419-1 international standards for emission test chambers and DIN ISO 16000-6 for VOC analysis.

It is absolutely vital to understand and comply with these standards before using the test method.

The objective of the test method is to achieve a reliable determination of the emission rate within the short printing time available, usually less than one hour, by means of a dynamic test chamber procedure with a well-defined air exchange rate. Various improvements in precision of the above-mentioned standards were necessary in order to obtain a practical test method.

Since the device materials themselves can emit certain VOCs, decreasing with time, the test method must also enable the measurement of VOC emission rates in the stand-by mode.

It must be understood that the measured emission rates are system-specific, since printers, photocopiers or multifunction devices show characteristic emission behaviour depending on the consumable materials used (especially toner and, in some conditions paper).

The measured emission rates may not exceed the permissible emission rates specified in the criteria for awarding the environmental label. They may also be used, for VOCs particularly, to estimate the resulting concentrations in model rooms or in real rooms.

It is generally assumed that the devices do not print continuously, that they are not designed to do so, but that they operate for a maximum of one tenth of a working day. Model calculations of Indoor air concentrations are, in reality, strongly influenced by adsorption effects on surfaces within the room, so that maximum concentrations will in reality be less than those calculated.

The test method was developed in the Federal Institute for Materials Research and Testing (BAM) within the framework of a research project supported by the Federal Environmental Agency (UBA) (Project No 201 95 311/02) with the technical support from other testing institutes, manufacturers, UBA and associations. A detailed description will be available in the final report to be published in the series of the UBA texts.

1. Definitions

Standby phase

With experimental set-up under normal climate conditions, the test object is located in the chamber, switched on and ready for use, so that printing can begin in the shortest possible time. The standby phase directly follows the conditioning phase without reopening the chamber.

Printing phase

Testing the test subject in printing mode under controlled atmospheric conditions directly after the standby phase without opening the chamber

Emission test chamber

A closed container with sampling and access ports and adjustable operational parameters for the determination of the emissions (VOC, ozone, dust) from printing and photocopying apparatus under an air flow.

Emission rate (product- or system-specific) SER_u [μg $piece^{-1}$ h^{-1}]

Product-specific (or system-specific, see preface) rate, which characterises the mass of the analyte (VOC, ozone, dust), emitted by the test object per unit time, at a particular point of time after the start of the test.

Volatile Organic Compounds (VOC)

In general: organic compounds which are emitted by the test subject and detected in chamber air. In the context of this method: identified and unidentified organic compounds, which elute between n-hexane and n-hexadecane, inclusive of these compounds, during gas chromatographic separation on a non-polar column.

Chamber loading

Placing a test subject in the test room.

Conditioning phase

With the Experimental set-up under normal atmospheric conditions, the test subject is conditioned in the chamber with paper already inserted, the power switch is switched to "on ", but the plug is not connected to the electricity supply. This technique allows the operator to put the device into the standby mode by inserting the plug into the socket without having to open the chamber.

Air exchange rate n [h^{-1}]

The ratio of the pure air volume brought into the emission test chamber in an hour, to the free volume in the same units of the empty emission test chamber, expressed in air changes per hour.

Air flow rate $V,^{\circ}$ [$m^3\ h^{-1}$]

Air flow rate supplied to the emission test chamber per unit time.

Air flow velocity v [ms^{-1}]

Air flow velocity over the surface of the test subject (distance 10 mm).

Secondary phase

With experimental set-up under normal atmospheric conditions, the test subject is still in the chamber, and the air exchange rate is the same as during the printing phase, but the printing cycle has just finished. The secondary phase follows directly on from the printing phase without opening the chamber.

Normal atmospheric conditions

Standard atmospheric conditions: 23 °C, 50 % relative humidity per ISO 554 [3].

Ozone half-life

The time that elapses whilst the ozone concentration decreases to half the initial concentration.

Test subject

Hardcopy device to be tested.

Total Volatile Organic Compounds (TVOC)

The total of the concentrations of identified and unidentified volatile organic compounds, which elute between n-hexane and n-hexadecane, inclusive of these compounds, during gas chromatographic separation on a non-polar column.

2. Measuring devices

- Emission test chamber as described in Section 4
- Atmospheric measurement devices with recorder as described in Section 4.1a
- Color mouse to produce print copies with 5 % black coverage as described in Section 4.1 b
- Current measuring instrument as described in Section 4.1 c
- Air sampling systems and adsorbents as described in Section 4.2
- Capillary gas chromatograph with a thermal desorption unit, coupled to a mass spectrometer with a detection unit as described in Sections 4.2 and 8.7
- Ozone analyser as described in Section 4.3
- Dust measurement area as described in Section 4.4

3. Test subjects

3.1 Selection

The client is responsible for delivery of the subjects. A device is usually a brand new prototype or taken from the current production series. The delivery contents are checked by the test laboratory and afterwards stored in the original packaging in an air-conditioned store (23 °C, 50 % R. H.). The measurement should take place as soon as possible, no more than ten working days after delivery at the latest.

3.2 Preparation of test subjects

Utility and suitability of the test subject are checked after delivery.

In particular, the manufacturer together with the test institute must ensure that the devices can be operated in the test chamber (By remote control via cables, mechanical trips or radio the it has to be sure that the printing process can be started from outside the chamber).

In agreement with the manufacturer, a printing mode has to be selected which enables maximum printing time. Capacities of the paper cassettes and paper stackers have to be considered. Power consumption in the standby phase and printing phase has to be determined. In addition the maximum printing time is determined with a sample printout of test pages (5 % surface black coverage). It is important that paper stacking takes place in a well organised way and if necessary, an additional receptacle made from inert material has to be used.

3.3 Consumable materials

Toner

The toner module supplied for any device should either be the manufacturers original configuration or compatible in type to that identified in the product documents. The testing institute has to be advised as to the exact specification of the toner so that a replacement of the same toner can be arranged.

Toners have to be stored according to the manufacturer’s specification prior to the test. (The toner can also remain in the device with agreement of the manufacturer.) The storage conditions are the same as for the test subject. Sufficient toner material and toner modules have to be made available.

Paper

The paper used for the tests must meet the requirements of DIN EN 12281 (2003-01) [5]. This standard demands a paper humidity between 3.8 % and 5.6 %. If the paper recommended by the manufacturer satisfies the standard this can also be used. The weight per unit area must be within the range of 70 to 80 gram per square metre. Paper humidity should be determined by DIN EN 20287 (1994-09) [8].

Paper humidity should not exceed 4 % for this type of test. Higher paper humidity can lead to condensation in the chamber during printing and make the use of larger chambers or larger air exchange rates necessary.

4. Measurements in emission test chambers

Emission test chambers and their specifications are described in [1], [2] and [6]. A chamber with a suitable volume has to be selected depending upon the size of the test subject to be examined.

The various ports must make good seals with the power cables and sensor lines passing through allowing VOC, dust and ozone to be sampled simultaneously. The test chambers must meet the requirements described in [6]. In particular this means:

- VOC-, ozone- and dust-free clean air supply
- Clean water supply
- Glass or special steel chamber walls
- Omission of sealing materials as far as possible
- Efficient air mixing

The following test conditions have to be adhered to by analogy with [6].

• Temperature	23 °C ± 2 K 1)
• Relative air humidity	50 % ± 5 % 1)
• Adjustable air exchange rate	
Large chamber ($V > 5\ m^3$)	$(1 \le n \le 2) \pm 5\%$
Small chamber ($V \le 5\ m^3$)	$(1 \le n \le 5) \pm 5\%$
• Air flow velocity	0.1 – 0.3 ms^{-1}

1) These atmospheric conditions cannot generally be maintained for the period shortly after loading the sample into the chamber and during the test in the printing phase.

Both 1 m³ chambers and large chambers with volumes > 5 m³ (e.g. 20 m³) make good emission test chambers [1]. Chambers are regarded as suitable if they adhere to the above conditions and exhibit sufficiently small blank values, in particular for VOC, ozone and dust, and ensure sufficiently large ozone half-lives.

Chambers must be checked for compliance with the test requirements before they are first used. The chamber blank values must stay below the following levels at an air exchange rate of n=1 h^{-1}:

Single substances	2 µgm^{-3}
TVOC	20 µgm^{-3}
Ozone	4 µgm^{-3}
Dust	10 µgm^{-3}

The ozone half-life of the chamber has to be checked at an air exchange rate of n = 1 h^{-1} by introducing a concentration of 0.1 to 0.2 ppm to the chamber. If the ozone half-life is at least ten minutes, the test chamber is suitable for ozone determination. However, if the ozone half-life is less than ten minutes, the chamber has to be cleaned in an appropriate way, until the target value is achieved. With air exchange rates other than n = 1 h^{-1}, different ozone half-lives occur.

Air exchange rates needed for the measurement have to be regularly checked and recorded with the chamber empty, by means of an independent procedure, e.g. tracer gas method per DIN V ENV 717-1 (1998) [4].

Test procedure (as per 8.1, flow diagram)

Blank values are determined before each measurement by setting an air exchange rate of $n = 1\ h^{-1}$ in the chambers, both for the conditioning phase and the standby phase. The printers are provided with sufficient toner and paper at the start of the conditioning phase. Measurements of the internal atmospheric conditions are recorded from the start of the conditioning phase. VOC measurements begin when the standby phase starts, then recording of ozone concentration can take place.

In large chambers after the end of the standby phase, the air exchange rate remains set at $n = 1\ h^{-1}$. In small chambers (1 to 5 m^3) the exchange rate is adjusted to a value of $n = 4 - 5\ h^{-1}$ (dry air, R. H. < 10 %) to keep relative air humidity below critical values, which otherwise rises due to water being given off by the paper during printing.

Under no circumstances must water condensation take place in the chamber, since this has an unacceptable influence on the measurement results.

VOC, ozone and dust sampling starts at the beginning of the printing phase and should carry on until the end of the secondary phase after printing. The secondary - phase runs over a period of four air exchanges (one hour with quadruple air exchange, and four hours with single air exchange). For small chambers an alternative or additional VOC sample has to be carried out at the end of the printing phase measurement (see Section 4.2), provided the printing phase takes at least ten minutes.

To determine the size of the chamber needed for the equipment, the following size range can be used:

$$0.01 < \frac{Vp}{V_K} < 0.25 \qquad (1)$$

V_P: volume of the test subject [m^3]
V_K: volume of the test chamber [m^3]

If in doubt, a smaller chamber size should be selected, since concentration values are higher and measurement uncertainty is reduced.

In contrast with previous practice, neither can the emission test chamber be opened nor are persons permitted to stay in the chamber during tests. Therefore, the test must be repeated when interruptions (e.g. a paper jam) occur. Such interruptions should be excluded as far as possible by careful preparation.

Quality assurance

Maintenance of quality-assurance standards when using the test method is an essential prerequisite for the determination of reliable emission rates. An overview of this subject can be found in the ECMA 328 standard [2, Section 9].

4.1 Atmospheric conditions, printer calibration, printer control

a) Atmospheric conditions

It is necessary to record atmospheric data over the entire sequence of the test cycle to analyse the measurement results. In addition a measuring system with attached data logger is needed. After calibration the following measurement accuracy must be achieved:

Temperature:	± 0.5 K
Relative humidity:	± 3.0 %.

In 8.5, two atmospheric curves from empty chambers and two climate curves from the printing phase are shown as examples. The calibrated Almemo 3290-8 device with climate recording facility and an FH A 646-R sensor of the Ahlborn company is one example of a suitable device for recording atmospheric data.

b) Printer calibration

A printing pattern with 5 % black coverage is used to prepare for emission tests on hardcopy devices. This print pattern is used in testing the yield of toner modules in accordance with DIN 33870 (2001-01) [9]. A linearised version of 16 equidistant grey tones of the testing device is used here (see 8.3).

The output is measured using, for example, a Color Mouse CM2C (Savvy Systems Limited, USA) and subsequent correction of the output files, to produce an appropriate print pattern with 5% black coverage (cf. 8.4). This file is saved for the test on a computer.

The information needed to produce the print pattern can be found on the following website: http://www.ps.bam.de/33870.

c) Printer control

The printing process has to be managed and controlled by means of the remote control capabilities of the test device as advised by the manufacturer. The operating conditions of the printer have to be recorded, especially in the standby and printing phases. This can be done by checking the power consumption of the test device using a multimeter (e.g. multimeter M 3850 M, Metex Corp., in the 20 A range, with data logger for electronic recording).

Measuring power consumption clearly shows the start and end of printing. Disturbances in operation are also recorded. Fig 8.8 shows an example of a power consumption record with the relevant operational phases indicated. Additionally, with access to the data network, the number of the printed pages can be requested, which is standard for modern printers.

4.2 VOC

VOC sampling is accomplished using Tenax with subsequent thermal desorption [7] and GC / MSD analysis. Samples are taken at the following points in time~~s~~ as a minimum:

a) Blank value shortly before loading the sample in the chamber

b) 20 minutes before the end of the one-hour standby phase (for 20 minutes with approx. 100 ml min^{-1})

c) From the start of the printing phase then continuously until the end of the secondary phase as a dual measurement and / or

d) Six minutes before the end of the ten- to thirty-minute printing phase (for five minutes with approx. 100 ml min^{-1}) as a dual measurement (one minute buffer time due to non-defined printing time)

If possible, all substances have to be identified and individually quantified using the relative response factors determined from a calibration by internal standard. For each measurement point, the sum of the concentrations must be calculated for all identified substances having retention time between n-hexane and n-hexadecane, and having $\geq$ 2 µg m^{-3} concentration. If substances cannot be identified or the relative response factor cannot be determined, quantification has to be performed based on the response factor of deuterated toluene.

The TVOC value should be calculated as the sum of the concentrations of all identified and unidentified substances, having $\geq$ 2 µg m^{-3} concentration, having retention time between n-hexane and n-hexadecane. Additionally, as described in [7], the TVOC value has to be calculated based on the response factor of toluene.

<u>Calculation of the emission rate during the standby phase</u>

The emission rate for the standby phase can be calculated from the concentration of the sample taken over the last twenty minutes of the one-hour phase using the equations:

$$SER_{u_R} = c_R * n_R * V \qquad (2) \qquad\qquad c_R = \frac{m_{VOC_R}}{V_S} \qquad (3)$$

c_R : VOC concentration [µg m^{-3}] during the standby phase

SER_{u_R} : VOC emission rate [µg h^{-1}] during the standby phase

m_{VOC_R} : Analysed mass [µg] of VOC during the standby phase

n_R : Air exchange rate [h^{-1}] during the standby phase

V: Volume of test chamber [m³]

V_S: Sample volume [m³] during the standby phase

Calculation of the emission rate during the printing phase

The emission rate during the printing phase can be calculated in two ways. These depend on the time of sampling:

a) Using the sample taken continuously from the start of the printing phase to the end of the secondary phase, the emission rate can be calculated using the following equation:

$$SER_{u_{PF}} = \frac{m_{VOC_{PF}} * n_{PF} * V * t_O}{t_P * V_S} \quad (4)$$

$SER_{u_{PF}}$: VOC emission rate [µg h^{-1}] determined from the printing and secondary phases

$m_{VOC_{PF}}$: Analysed mass [µg] of VOC during the printing phase and secondary phases

n_{PF} : Air exchange rate [h^{-1}] during the printing and secondary phases

t_P: Absolute printing or copying time [min]

t_O: Overall sampling time [min]

V: Volume of test chamber [m³]

V_S: Sample volume [m³] during the printing and secondary phases

b) Using the sample taken six minutes before the end of the printing phase. The emission rate can be calculated by the following equation, which is however only applicable to small chambers with high air exchange rates, and a minimum of ten minutes printing time:

$$SER_{u_P} = \frac{c_P * V * n_P}{1 - e^{-n_P * t}} \quad (5)$$

c_P : VOC concentration [µg m^{-3}] during the printing phase

SER_{u_P}: VOC emission rate [µg h^{-1}] determined from the printing phase

n_P : Air exchange rate [h^{-1}] during the printing phase

V: Test chamber volume [m³]

t: Medium time of sampling [h], calculated from start of printing (e.g.: sampling interval from minute 5 (t_1) to minute 10 (t_2); t = 0.5 * (t_1 + t_2) = 0.125 h (7.5 minutes))

The sampling and analysis procedure described in 8.7 is suitable for a broad range of emitted compounds. A list of compounds that can occur in emission measurements on printing and photocopying devices, is also given in 8.7.

4.3 Ozone

The measurement procedure is based on a flameless reaction between ozone and ethylene. The chemoluminescence produced can be measured photometrically. Ozone emission testing of printers and copiers has to be performed as follows:

a) Determination of the blank value.

b) Determination of the ozone concentration in the standby phase. Recording of the ozone concentration can already take place here.

c) Ozone determination during printing / copying:

Ozone determination starts immediately at the beginning of the printing job and continues until the end of the secondary phase. The concentration should be recorded every 30 seconds at least, or better still, at every 15 seconds. If a suitable concentration range has been selected, the ozone concentration can be recorded permanently using an electronic data logger.

Ozone half-life can be determined from the decay curve in the secondary phase, where a good approximation of the conditions of the print job still prevails. Ozone emission rate can be calculated using the following equations:

$$SER_u = \frac{c_{\max} * k' * V * p}{T * R} \qquad (6) \qquad\qquad k' = \frac{\ln 2}{H'} \qquad (7)$$

SER_u: Ozone emission rate [µg or mg unit time^{-1}]
$c_{\max}$: Maximum ozone concentration [µg m^{-3}]
k': Proportionality factor [min^{-1}]
H': Ozone half-life under test conditions [min]
V: Volume of test chamber [m^3]
p: Air pressure [Pa]
T: Absolute temperature [K]
R: Gas constant [Pa K^{-1}], (339.8 [Pa K^{-1}] for ozone)

For very small ozone emission rates the determination of the ozone half-life is difficult under test conditions. However, to facilitate an analysis, ozone can be injected into the chamber after the print job and secondary phase and the ozone half-life so determined. Thus the chamber remains loaded. The printed paper also remains in the test room. Atmospheric conditions, in particular the air exchange rate, remain as during the printing test. An approximate but usable ozone half-life value can be determined under these conditions. Calculation can then be performed using the above equations.

Example for an ozone test instrument

Model 3010 Ozonanalysator (ozone analyser). Manufacturer: UPM, Umwelt Pollution-Messtechnik (Environment Pollution Measurement Techniques). This gives continuous determination of ozone concentration.

4.4 Dust

Dust emission rate is determined using the gravimetric method.

Sampling

Air sampling is performed over a defined time interval (printing and secondary phase). During this time interval, air pumped from the test chamber is drawn through a glass-fibre filter. The volume of air drawn through the filter is measured (in m^3). The absolute weight of dust is obtained in µg by differential weighing of the filter. From both values, dust concentration in the test chamber (in $\mu g * m^{-3}$) can be calculated and from this the specific emission rate (in $\mu g * h^{-1}$).

Standard conditions for gravimetric dust measurement

Dust filter:	Glass-fibre filter with appropriate mounting plate
Sampling point:	Centre of the chamber wall
Volume Sampling - rate:	Up to 90 % of the air flow rate in the chamber during the sampling phase
Sampling time:	Total printing and secondary running time

Procedure for gravimetric dust measurement – moisture correction

The glass-fibre filters (measuring filters), used for gravimetric dust measurement, must be stored in an air-conditioned room (weighing room) before the measurement and must be conditioned in the prevailing climate until the mass is constant. Since even the slightest unavoidable fluctuations in the relative humidity of the weighing room affect the mass of the glass-fibre filters, at least one empty glass-fibre filter (reference filter) is weighed at the same time as the measuring filters, before dust sampling (tare weight). Through this correction the influence of the atmospheric conditions on the filter mass is minimized.

Climate conditions in the weighing room:

Temperature:	23°C ± 2 K
Relative humidity:	50 % ± 5 %

During dust sampling in the test chamber air is drawn through the measuring filter. Since the relative humidity of this air can deviate from that in the weighing room, the measuring filter must be returned to the weighing room after dust sampling, and again conditioned to constant mass.

The reference filter remains in the weighing room and is re-weighed when the dust filter weighing (gross weight) is carried out. The mass difference between the first and the second weighing of the reference filter is due to climate changes and is subtracted from or added to the gross mass of the measuring filter.

Determination of absolute dust weight on the measuring filter (moisture correction)

$$m_{Dt} = (m_{MF_{gross}} - m_{MF_{tare}}) + (m_{RF_1} - m_{RF_2}) \qquad (8)$$

m_{Dt} : Weighed mass of dust (moisture-corrected) [µg]

$m_{MF_{gross}}$: Mass of conditioned measuring filter after dust sampling [µg]

$m_{MF_{tare}}$: Mass of conditioned measuring filter before dust sampling [µg]

m_{RF_1} : Mass of conditioned reference filter weighed at the same time as measuring filter before dust sampling [µg]

m_{RF_2} : Mass of conditioned reference filter weighed at the same time as measuring filter after dust sampling [µg]

Calculation of dust concentration and emission rate

$$SER_{u_{Dt}} = \frac{m_{Dt} * n_{PF} * V * t_O}{V_S * t_P} \qquad (9) \qquad\qquad c_{Dt} = \frac{m_{Dt}}{V_S} \qquad (10)$$

c_{Dt} : Dust concentration in test chamber [µg m^{-3}]

$SER_{u_{Dt}}$: Dust emission rate [µg h^{-1}]

m_{Dt} : Weighed mass of dust (moisture-corrected) [µg]

n_{PF} : Air exchange rate [h^{-1}] during the printing and secondary phases

t_P : Total printing or copying time [min]

t_O : Overall sampling time [min]

V : Volume of test chamber [m³]

V_S : Volume of air sucked through glass-fibre filter [m³]

Example for a gravimetric dust measurement method

Ultramicro scale: Type UMX2/M

Pump: Müller inc. GSA 50

Gas flow rate meter: Schlumberger inc. REMUS 4 G 1,6

Glass-fibre filter: Schleicher & Schuell inc., diameter 50 mm

5. Evaluation and test report

The test and analysis of the test subject must both be fully documented in the test report.

The following data have to be included:

- Manufacturer,
- Exact product description, device number, exact toner description, and description of paper used,
- Date of manufacture,
- Date of delivery,
- Type of packaging,
- Storage prior to measurement,
- Test date/time period,
- Calibration of equipment,
- Test conditions (type and size of chamber, temperature, relative humidity, air pressure, air exchange rate or air flow rate),
- Duration of printing job,
- Number of pages printed,
- Time and interval of air sampling, volume and flow rate of air sampling for VOC, ozone and dust,
- Name, CAS-No. and concentration of identified VOCs, as well as concentration of unidentified VOCs in standby phase and printing phase, and calculated emission rates. Benzene and styrene have to be separately listed in every case.
- The TVOC value calculated as the sum of the concentrations of all identified and unidentified substances, additionally the TVOC value calculated based on the response factor of toluene,
- Ozone half-life of empty chamber and from the secondary phase,
- Ozone concentration and calculated ozone emission rate during printing,
- Dust mass measured gravimetrically and dust emission rate calculated from it,
- Detection limits of VOC-, dust- and ozone emission rates,
- Disruptions and deviations from test algorithm,
- Summary of the results by the testing institute with respect to environment label criteria (if necessary, indication that the determined emission characteristic is only valid in connection with the tested toner type)

6. Test institutes

Emission tests may be performed by suitable institutes only.

Test institutes are considered to be suitable if they have the necessary apparatus and a quality management system (or are accredited in the field of these tests) and have proved their expertise for these tests by successfully participating in relevant co-operative tests or comparative measurements. The same applies to the testing laboratories of manufacturers.

The proof of adherence to these requirements can be provided to the Federal Institute for Materials Research and Testing, Division "Environmental Material and Product Properties/Emission from Materials ". In the case of present suitability, this is confirmed in writing.

7. Literature

[1] Entwicklung einer Prüfmethode und Untersuchungen zur Begrenzung von Emissionen aus Druckern und Kopiergeräten im Rahmen der Umweltzeichenvergabe. (Development of a test method and investigation into limiting emissions from hardcopy devices within the framework of an environmental label award.) UBA-Project-No. 201 311/02, Federal Institute for Materials Research and Testing (BAM), Final report (in print), Berlin 2003

[2] ECMA-Standard 328, Detection and measurement of chemical emissions from electronic equipment, August 2001 (org)

[3] ISO 554, Edition:1976-07 Normalklimate für die Konditionierung und / oder Prüfung; Anforderungen (Standard atmospheres for conditioning and/or test; Requirements)

[4] DIN V ENV 717-1, (Pre-standard) Edition:1999-02 Holzwerkstoffe - Bestimmung der Formaldehydabgabe - Teil 1: Formaldehydabgabe nach der Prüfkammer-Methode (Wooden materials - Determination of formaldehyde emission - Part 1: Formaldehyde emission per the test chamber method); Deutsche Fassung (German Version) ENV 717-1:1998

[5] DIN EN 12281, Edition: 2003-01 Druck- und Büropapier - Anforderungen an Kopierpapier für Vervielfältigungen mit Trockentoner (Printing and office paper – Requirements of copying paper for photocopying with dry toner); Deutsche Fassung (German Version) EN 12281:2002

[6] DIN V ENV 13419-1, (Pre-standard) Edition: 1999-10 Bauprodukte - Bestimmung der Emission von flüchtigen organischen Verbindungen (VOC) - Teil 1: Emissionsprüfkammer-Verfahren (Building products - Determination of the emission of volatile organic compounds (VOC) - Part 1: Emission test chamber procedure); Deutsche Fassung (German Version) ENV 13419-1:1999

[7] DIN ISO 16000-6: Innenraumluftverunreinigungen. Teil 6: Bestimmung von VOC in der Innenraumluft und in Prüfkammern. Probenahme auf TENAX TA, thermische Desorption und Gaschromatographie/MSD bzw. FID (Indoor air pollutions. Part 6: Determination of VOC in indoor air and in test chambers. Sampling on TENAX TA, thermodesorption and gaschromatography/MSD or FID) (ISO/DIS 16000-6:2000). Draft September 2002

[8] DIN EN 20287, Edition: 1994-09 Papier und Pappe - Bestimmung des Feuchtegehaltes - Wärmeschrankverfahren (Paper and cardboard - Determination of humidity content - Warming cupboard procedure) (ISO 287:1985); Deutsche Fassung (German Version) EN 20287:1994

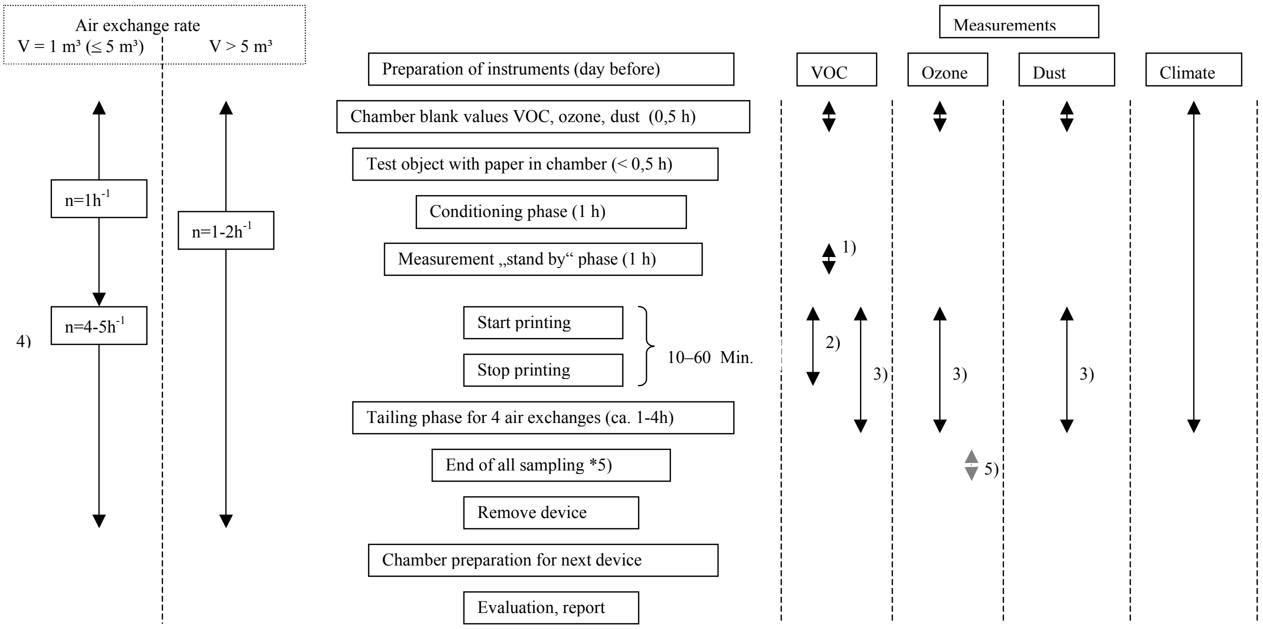
[9] DIN 33870, Edition: 2001-01 Informationstechnik - Büro- und Datentechnik - Anforderungen und Prüfungen für die Aufbereitung von gebrauchten Tonermodulen schwarz für elektrophotographische Drucker, Kopierer und Fernkopierer (Information technology - Office and data processing technology - Requirements and tests for the processing of used black toner mo-

dules for electrophotographic printers, copiers and telecopiers)

[10] O. Jann, O. Wilke, R. Noske, D. Brödner, U. Schneider, J. Rockstroh, W. Horn: Investigations of VOC-, ozone- and dust-emissions from printers in test chambers. Healthy Buildings 2003, Singapore, Dezember 2003, submitted for presentation.

8. Illustrations and examples

8.1 Test flow diagram



1) Sampling over last 20 minutes (100 ml / Min.)

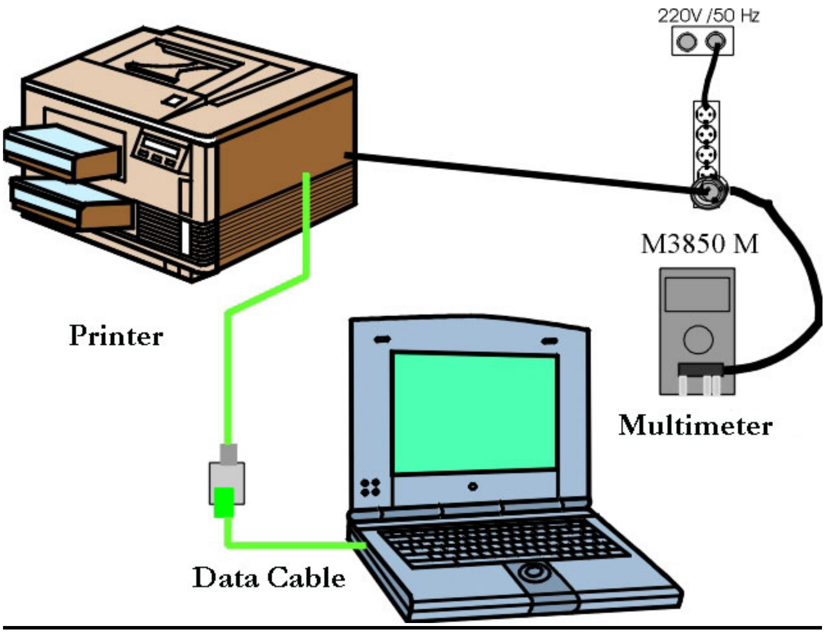
2) Sampling over last 5 minutes (100 ml / Min.)

3) Continuous sampling

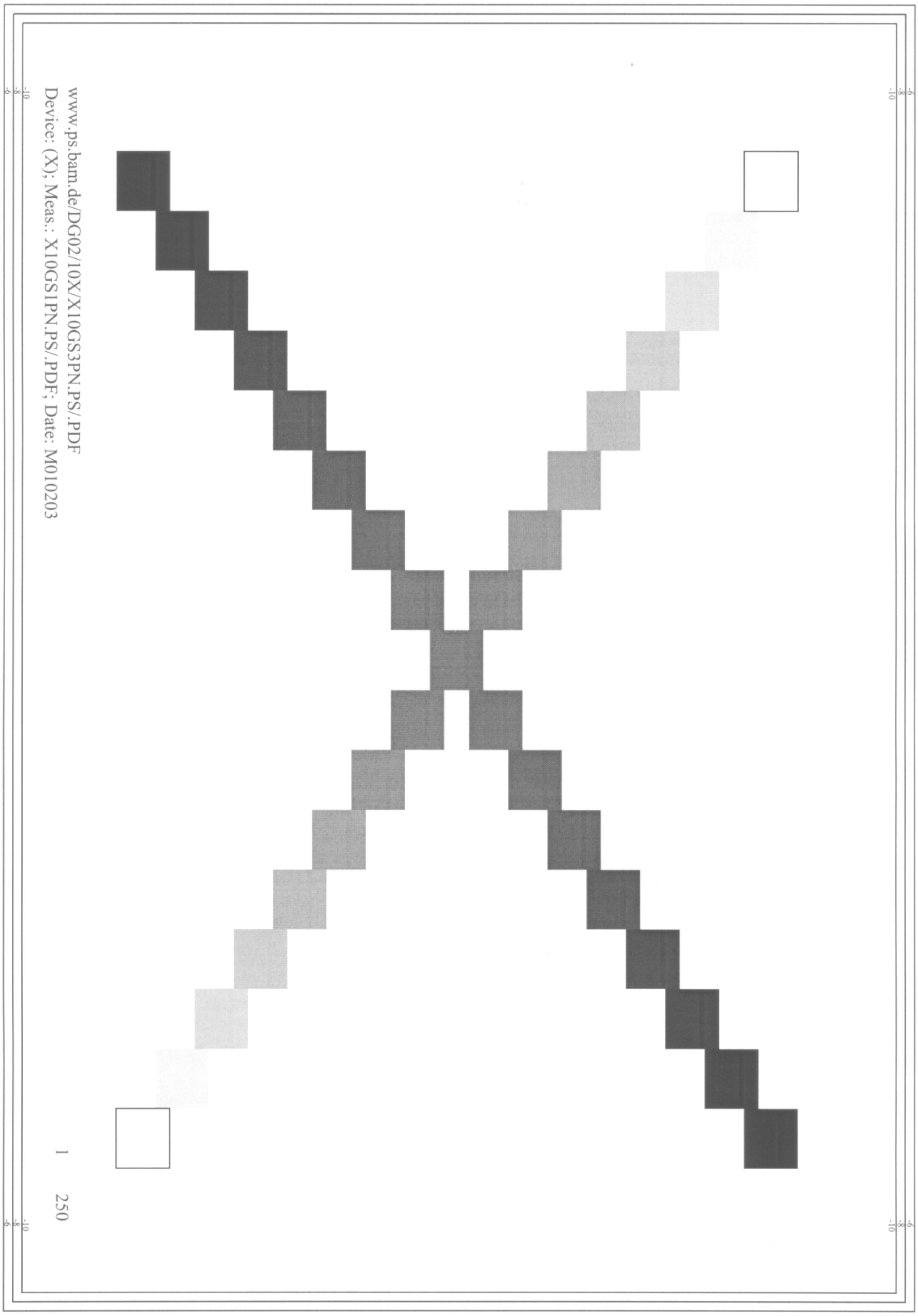
4) Dry feed air flow(< 10 % r.h.), air exchange rate has to be known and steady

5) Possibly separate determination of ozone half life, if not ascertainable from the concentration descent after end of printing, approx. 1 h

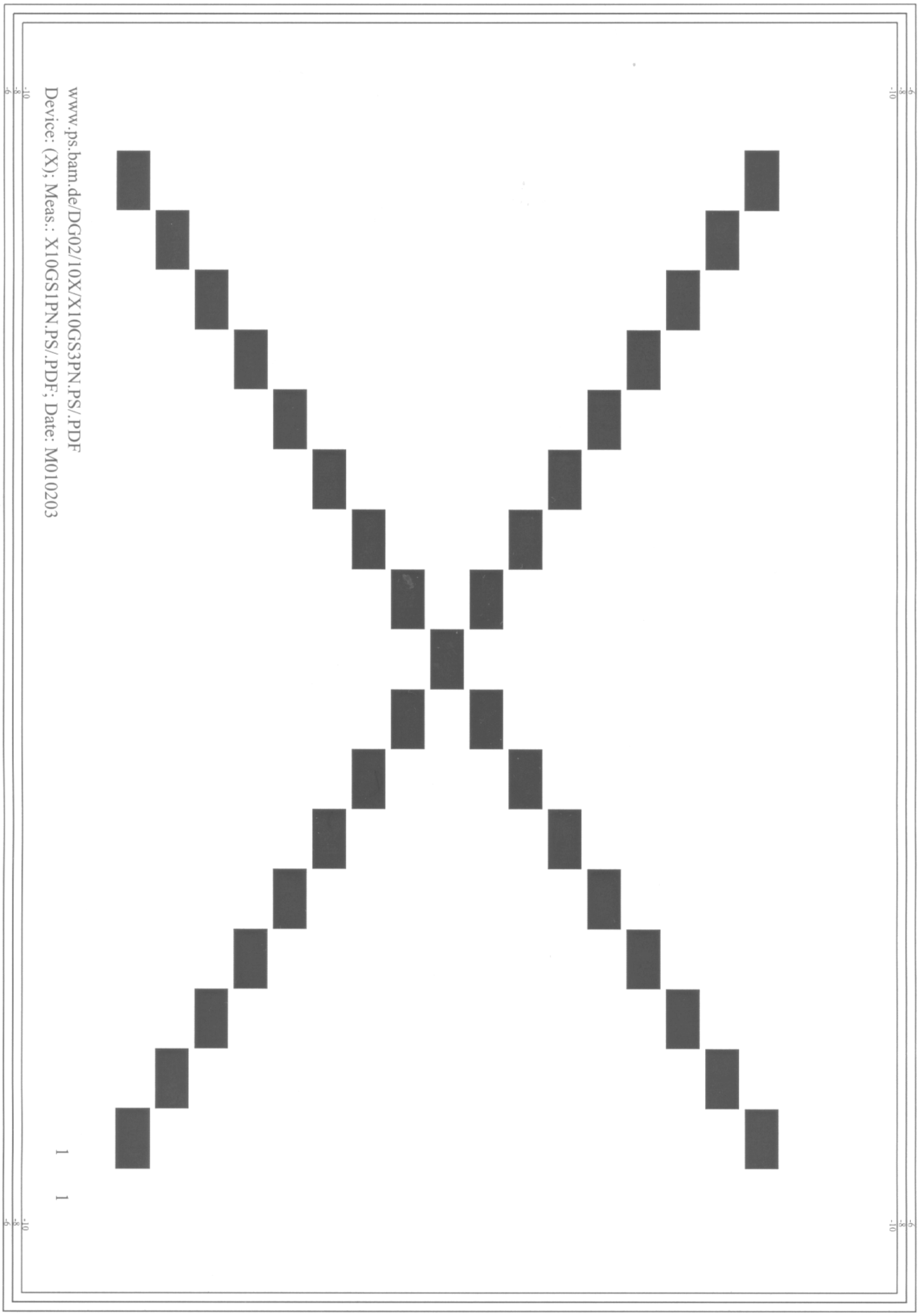
8.2 Measurement set-up for devices



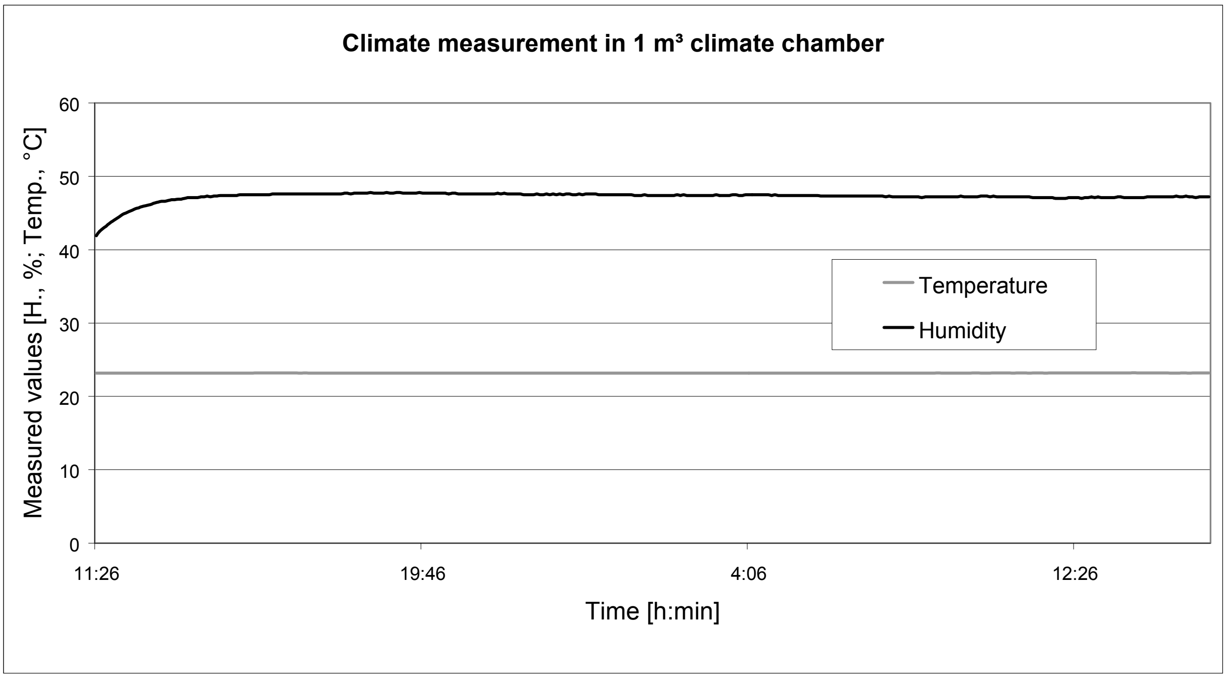
8.3 Grey scale linearisation pattern for the 5 % print master

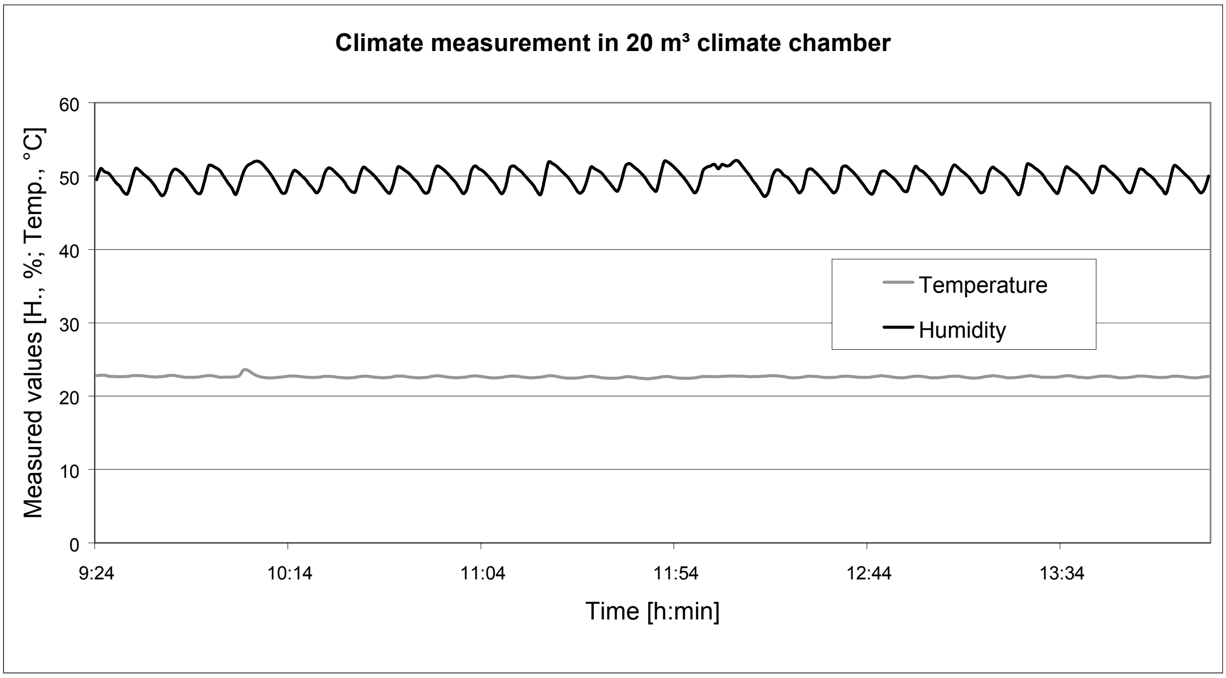


8.4 Master print pattern 5 % black coverage, per DIN 33870



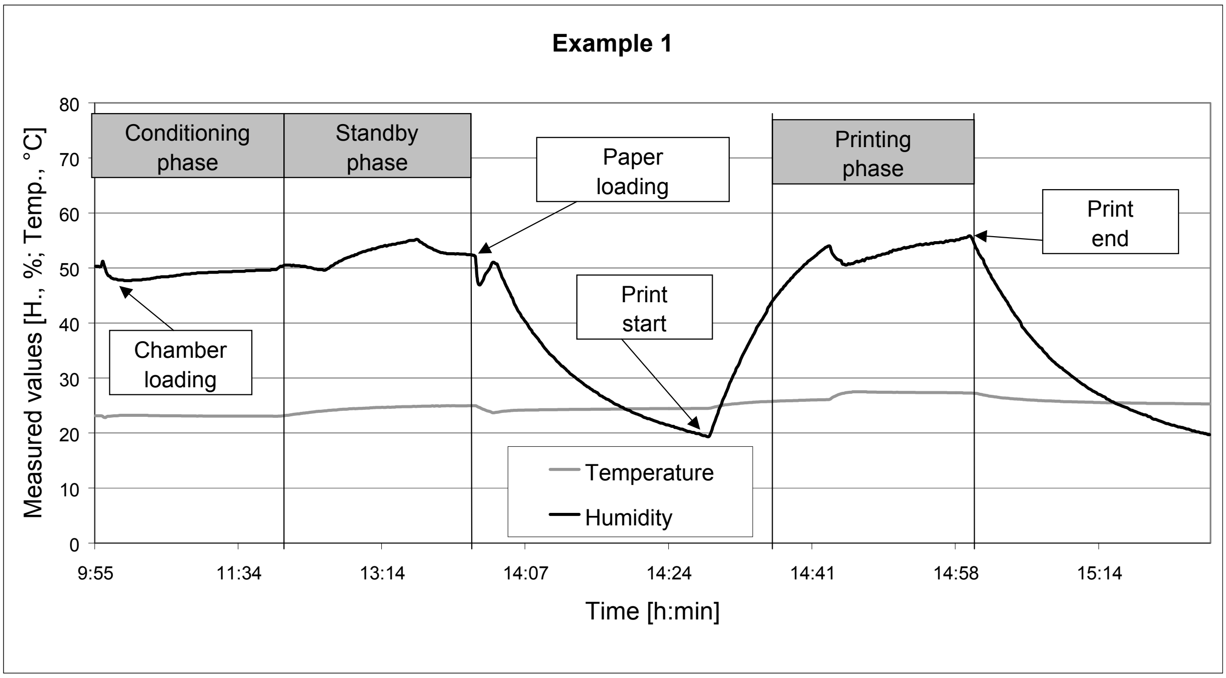
8.5 Examples of atmospheric measurement (empty chamber)

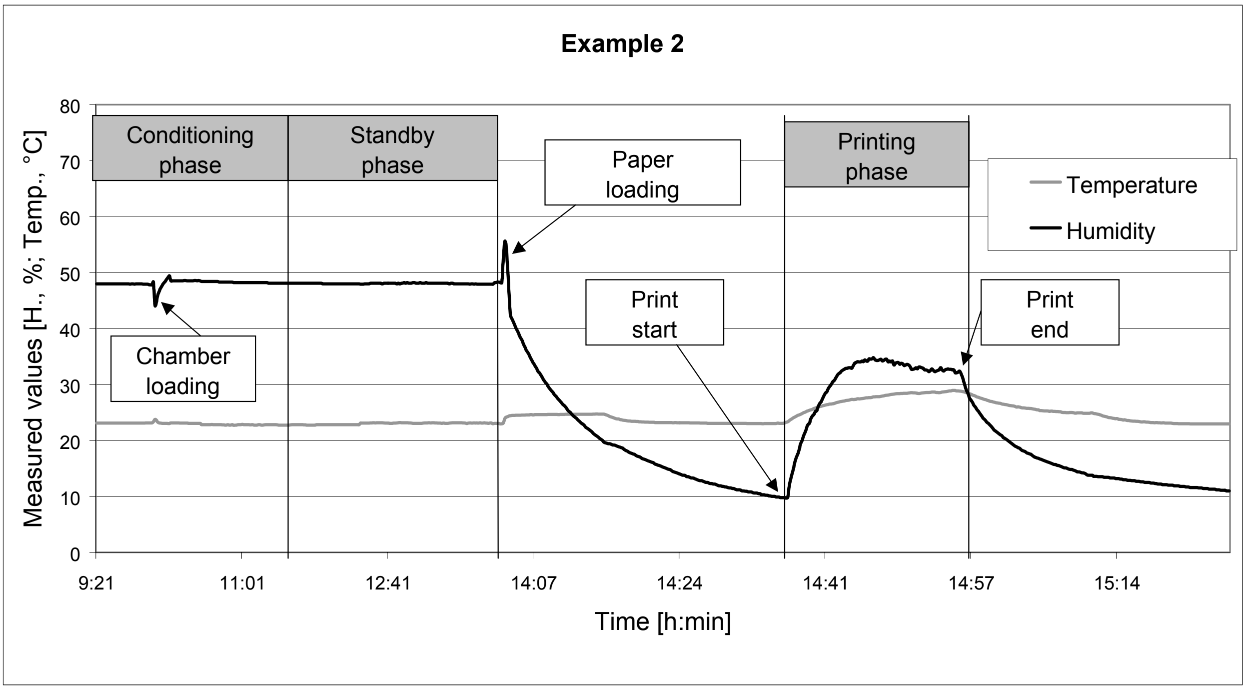




8.6 Atmospheric curves in the tests

(Conditioning and standby phases are each 2 hours in these examples)





8.7 Example of a proven measurement method ([2], [4])

Sampling pipes: Tenax TA (tube length 178 mm, OD 6 mm, ID 4 mm, 200 mg Tenax TA (60-80 mesh) with glass wool plug); Sampling flow rate > 0.5 l (100 ml/min). Before sampling the Tenax pipes have to be spiked using (deuterated) toluene diluted in methanol as an internal standard.

The calibration is performed in such a way that the calibration substances, dissolved in methanol, are applied (spiked) to separate Tenax pipes. Also, to simulate sampling, 1 l sample air is extracted from an empty chamber, and at the same time methanol remaining on the Tenax after spiking is desorbed.

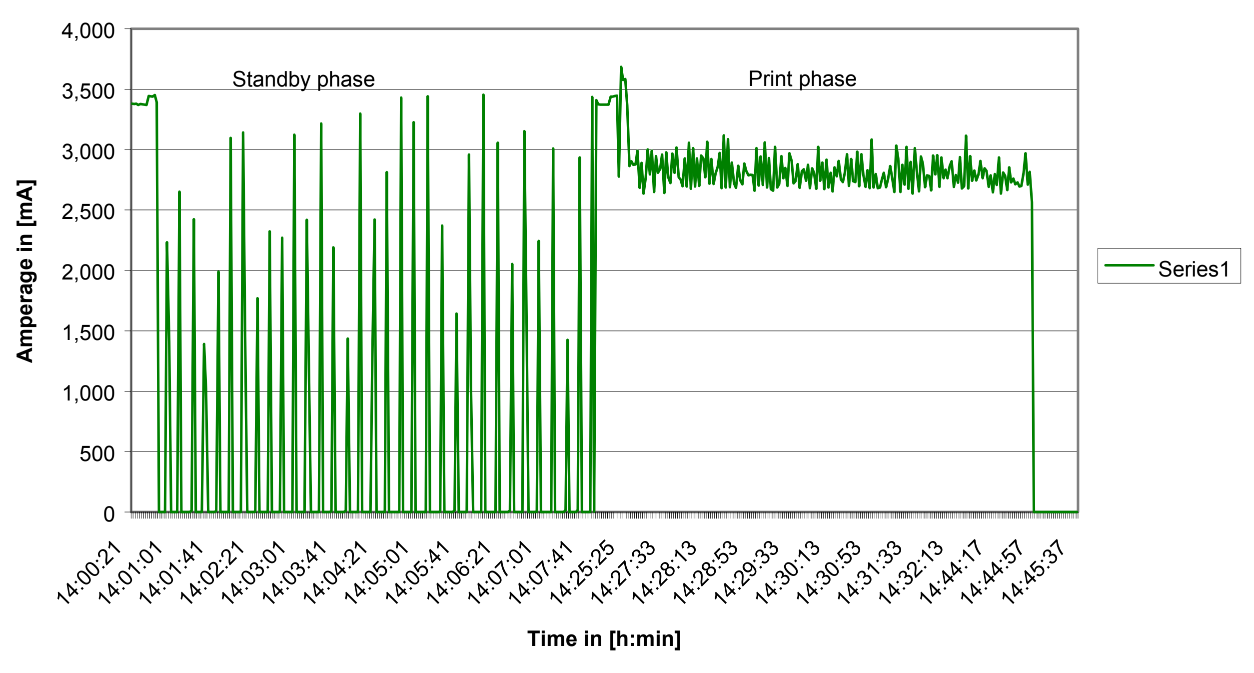
Analysis system: Gerstel TDS-2 / KAS-3 thermal desorption/cold feed system (program 40-280°C with 40°C/min, keep 5 min at 280°C / at -150 °C, heating with 10°C/s up to 290°C / He flow 35 ml/min)

HP GC 5890 II + / HP-MSD 5972 (column HP 1; 60 m; 0.25 mm; 0.25 µm; temperature program 40°C for 4 min, 5°C/min up to 140°C, 10°C/min up to 240°C, 25°C/min up to 290°C, keep for 3 min / MSD: scan 25 - 400; 1.9 scans/s; 300°C; NBS-75k - database)

Potential compounds

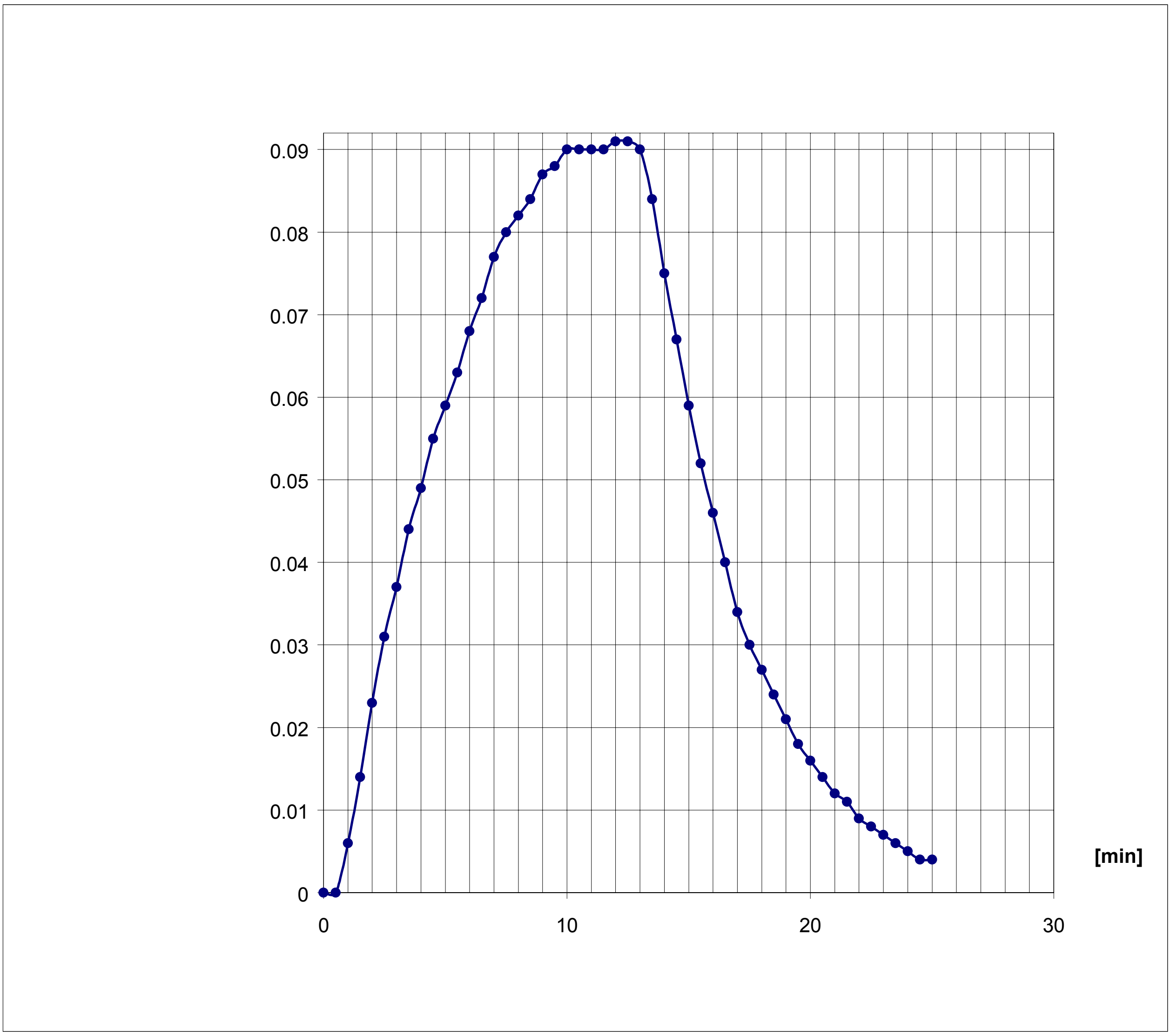
Acetophenone
Benzaldehyde
Benzene
BHT
Biphenyl
Butanone
Δ3-Carene
Ethylbenzene
Ethyleneglycol
Ethylhexanol
Heptanal
Hexadecane
Hexanal
Iso-alcane
Iso-propylbenzene
n-Butanol
n-Pentanal
n-Propylbenzene
Nonanal
Octanal
Pentadecane
Phenol
Propyleneglycol
Siloxane (e.g. D3-D6)
Styrene
Toluene
Xylene (m, o, p)

8.8 Power consumption of the test subject



8.9. Ozone concentration during printing

a) High concentration (data in ppm)



For the calculation of the emission rate the ozone half-life can be determined from the trailing slope of the ozone concentration curve (after the end of the printing cycle).

8.9 Ozone concentration during printing

b) Low concentration (data in ppm)