Aerosol emission from cleaning sprays

Design and evaluation of a generation and characterization system for spray aerosols and a human pre-exposure study

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Bättre lite skit i hörnen än ett sprejstädat hem?
Populärvetenskaplig artikel

Text: Karin Lovén
EAT, Designvetenskaper, Lunds universitet
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Städsprejer används av allt fler, både hemma och på arbetsplatser. Den senaste forskningen visar dock att användning av städsprejer kan leda till akuta hälsoeffekter, både i näsa och i ögon.

I Sverige är städare det tionde vanligaste yrket med mer än 70 000 anställda varav mer än 75 % är kvinnor. Städpersonal är dock utsatt för flera arbetsrelaterade riskfaktorer, däribland hög belastning på skelett och muskler och problem med luftvägarna. Som en del i ett forskningsprojekt vid Lunds universitet har en mindre exponeringsstudie nyligen genomförts. Åtta frivilliga försökspersoner exponerades för olika doser av en fönsterputssprej. Försökspersonerna fick själva putsa ett fönster i en kammare med kontrollerat luftflöde och partikelfiltrering.

Hälsoeffekterna utvärderades sedan med hjälp av tre olika metoder, ett frågeformulär och två medicinska undersökningar. I formulären fick försökspersonerna själva fylla i om de kände av några besvär i näsan, ögonen eller halsen, både före, under och efter sprejningen. Den första medicinska undersökning som genomfördes var en mätning av det maximala luftflöde som försökspersonen kan uppnå genom att andas in genom näsan, en så kallad PNIF-mätning. Denna mätning gjordes både före och efter varje sprejning och gav ett mått på hur påverkad näsan blir av exponeringen. Den andra undersökningen var en mätning av hur lång tid det tar för ögonens tårfilm att börja spricka upp, en så kallad BUT-mätning. Denna gjordes före den första sprejningen och sedan efter varje sprejdos och gav ett mått på hur torra ögonen blev.

Från denna studie kunde ett par trender identifieras. Exempelvis minskade BUT-tiden när spraydosen ökade, vilket innebär att tårfilmen påverkas av sprejningen och ögonen blir torrare. En annan trend som kunde ses var att försökspersonerna verkade uppleva starkare symptom i näsan i takt med att sprejdoserna ökade, en påverkan som dock inte kunde ses i PNIF-mätningarna.

När städsprejerna används bildas vätskedroppar av rengöringsmedel, så kallade aerosoler, vilka sprids i luften. Som en del i projektet undersöktes även hur stor del av den vätska som sprejades ut från flaskan som faktiskt hamnade på väggen (mot vilken sprejningen gjordes) och hur stor del som förblev i luften och därmed kunde andas in. Mätningar gjordes även för att undersöka hur stora vätskedropparna var, direkt när de kommer ut från sprejmunstycket, men också hur små partiklarna blivit efter att de torkat ett par sekunder i luften. Totalt undersöktes sex olika rengöringsprodukter.

Resultaten från dessa mätningar visade att mycket av fönsterputssprejerna stannade kvar i luften, mellan 9 och 16 % av det som sprejades ut från flaskan, i jämförelse med produkterna för fläckar och allmänna ytor. Av dessa förblev endast mellan 3 och 5 % i luften efter sprejning. Dessutom förångades mer än 99,9 % av vätskan från de ursprungliga dropparna (för alla testade produkter) snabbt till gas och storleken på de kvarvarande, torkade partiklarna var mellan 2 och 4 µm.

Vidare forskning inom området behövs, men förhoppningen är att rekommendationer och riktlinjer för städsprejanvändning ska kunna fastslås inom en snar framtid.

Acknowledgements

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I have been working together with a few people at the department, foremost PhD Anders Gudmundsson (examiner) and PhD Christina Isaxon (main supervisor), but with some additional help in the lab from Jonas Jakobsson and input and advice from PhD Aneta Wierzbicka (assistant supervisor). The pre-exposure study was conducted together with MD PhD Jörn Nielsen from the division of Occupational and Environmental Medicine at Lund University and MD PhD Gunilla Wieslander from the division of Occupational and Environmental Medicine at Uppsala University. I would like to thank all of you for all the help during my work with the thesis and for the opportunity to work with and learn from you.

Karin Lovén
March 2015

Abstract

In Sweden, the 10th most common occupation is professional cleaning. Cleaning workers are exposed to many risk factors including high physical workload and the development of new-onset asthma and other types of respiratory symptoms. This master thesis has been a part of a research project at the division of Ergonomics and Aerosol Technology (EAT), Lund University, in which the health aspect of cleaning workers with regards to ergonomic load and airway exposure, when using spray bottles compared to traditional cleaning with cloth and bucket, is being investigated. The main objectives of this thesis have been to identify and characterize the most common spray cleaning products used by cleaning workers in Sweden, and to design a human pre-exposure study to determine dose-response relationships.

The identification of cleaning products was done by a phone survey and based on the responses from this survey six products, for the use in bathrooms, on windows, on stains and for all surfaces were selected. Aerosol characterization of the products was done by two main methods, determining the airborne mass fraction and the particle/gas ratio.

The airborne mass fraction was measured using a paper-setup. The cleaning product was sprayed at a paper taped on the wall and the mass of the bottle and of the paper was weighed before and after spraying, to determine how much mass that remained airborne, the airborne mass fraction.

The particle/gas ratio was determined by measuring the concentration increase during product use, in turn determining the source strength for the particles. This was compared to the total source strength (for the bottle) and the source strength for the surface (obtained from the airborne mass fraction) to determine the particle/gas ratio.

The two window cleaning sprays had a high airborne mass fraction (9.1 and 15.7 % respectively) compared to the sprays for stains and all surfaces (2.7 and 4.9 % respectively). However, the mass percentage of particles suspended in the air after spraying, for all products, was very low. More than 99.9 % of the initial spray droplet mass would evaporate to a gaseous phase. The mass median diameters measured with the APS (for the dried particles) were 1.8-4.2 µm for all products.

The human pre-exposure study showed no statistical connections due to the limited number of subjects and the large individual variations, but some trends could be seen. For example that the tear film break up time decreased with increasing spray dose, suggesting that the tear film is destabilizing with increased exposure to a window cleaning spray. An increase in nose symptoms could also be observed with increasing spray dose.

Sammanfattning

I Sverige är städare det tionde vanligaste yrket. Städpersonal är utsatt för flera riskfaktorer inklusive hög arbetsbelastning och utveckling av astma eller andra typer av luftvägsproblem. Detta examensarbete har varit en del av ett forskningsprojekt på avdelningen för Ergonomi och Aerosolteknologi (EAT), Lunds universitet, vars syfte är att undersöka städares belastning på rörelseorganen och luftvägsexponering för rengöringsprodukter, med speciellt fokus på betydelsen av sprayanvändande. Huvudsyftet för detta examensarbete var att identifiera och karaktärisera de vanligaste rengöringssprayerna som används av städpersonal i Sverige samt att designa en human exponeringsförstudie med syfte att bestämma dos-respons förhållanden.

Identifieringen av rengöringsprodukter gjordes genom telefonintervjuer och baserat på svaren från dessa valdes sex produkter ut, för användning i badrum, på fönster, på fläckar och för allmänna ytor. Aerosolkaraktäriseringen bestod framförallt i att bestämma den luftburna massfraktionen och partikel/gas förhållandet.

Den luftburna massfraktionen mättes med hjälp av en uppställning baserad på papper. Rengöringsprodukten sprayades mot ett papper upptejpad på väggen och massan för flaskan och för pappret vägdes före och efter sprayningen för att bestämma hur mycket massa som stannade kvar i luften, den luftburna massfraktionen.

Partikel/gas förhållandet bestämdes genom att mäta koncentrationsökningen under tiden som produkten användes för att med hjälp av detta bestämma källstyrkan för partiklarna. Detta värde jämfördes sedan med den totala källstyrkan (för flaskan) och källstyrkan för ytan (beräknat från den luftburna massfraktionen) för att bestämma partikel/gas förhållandet.

De två fönstersprayerna visade på en hög luftburen massfraktion (9,1 respektive 15,7 %) jämfört med sprayerna för fläckar och allmänna ytor (2,7 respektive 4,9 %). Dock visade det sig att massprocenten av partiklar i luften efter sprayning, för alla produkter, var mycket låg. Mer är 99,9 % av massan för begynnelsedroppen (precis utanför spraymunstycket) förångades till gasfas. Massmedian diametrarna som uppmättes med APSen (för de torkade partiklarna) var 1,8-4,2 µm för alla produkter.

Den humana exponeringsförstudien visade inga statistiskt signifikanta samband eftersom antalet försökspersoner var begränsat samt att det förekom stora individuella variationer, men några trender kunde identifieras. En av dessa trender var en minskande tårfilmsstabilitet med ökande spraydos. Ökande nässymptom med ökande spraydos kunde också ses i resultaten.

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1. Introduction

Professional cleaning is the 10th most common occupation in Sweden with more than 70 000 workers employed in 2012 and more than 75 % of them are women (SCB 1, 2014). Cleaning workers are exposed to many risk factors such as high physical workload causing musculoskeletal disorders in the neck, shoulders, elbows and hands (Unge et al., 2007; Hansson et al., 2009; Hansson et al., 2010). In 2014, 11.7 % of the female cleaners in Sweden experienced problems with their shoulders and arms compared to 7.1 % of females in all the occupations listed in the survey. 6.7 % of the female cleaners also experienced problems with their hands and fingers compared to 2.5 % of the females in all the occupations listed (SCB 2, 2014).

The use of spray bottles can be assumed to be a more preferable cleaning method with regards to musculoskeletal load. This since a lot of heavy tasks, such as measuring, pouring and mixing cleaning products in buckets, can be avoided. Spray as an application method is also a fast and easy way to clean and gives an even and precise dosage of cleaning product. It is therefore a relevant assumption that the use of cleaning sprays is increasing and will continue to increase in the future.

A survey report (EPHECT, 2012) from the EU project EPHECT (Emission, Exposure Patterns and Health Effects of Consumer Products in the EU) present the user patterns of consumer products. According to this report, cleaning products for universal use, kitchen, bathroom and windows were the most commonly used products (of the ones included in the survey) across the European market. In Swedish households these products were used to the same, or even greater extent with 86, 83, 76 and 74 % respectively of the respondents using these products during the six months before the survey. Furthermore, using these products as sprays is more common in Sweden than compared to the average in the EU with 54, 77, 75 and 73 % respectively, compared to the EU average of 47, 54, 51 and 67 % respectively. The most common brand for cleaning products for universal use, bathroom and windows across the whole EU was Ajax and this brand was also the third most common brand for kitchen cleaning products.

Another risk factor for cleaners is the development of new-onset asthma and other types of respiratory symptoms due to exposure to cleaning products (Lillienberg et al., 2012; Kogevinas et al., 2007). In Sweden in 2014, 3.7 % of the female cleaners were suffering from work-related allergy including asthma compared with 1.6 % of females in all the occupations listed in the survey (SCB 2, 2014). Furthermore, there are studies (Nielsen, 1999; Zock 2001; Zock 2007) that show a correlation between the use of cleaning sprays and the development of new-onset asthma as well as other respiratory symptoms.

The general purpose of this master thesis work was to identify and characterize the most common cleaning products applied by spray used by cleaning workers in Sweden as well as study some health effects during cleaning spray use. The more specific objectives of this master thesis work were to:

- do a phone based survey with a selection of Sweden's cleaning companies to identify which cleaning sprays are the most frequently used,
- based on the phone survey, select products for characterization,
- design an experimental setup for characterizing the airborne mass fraction for the selected products and perform these measurements,

- design an experimental setup for characterizing the particle/gas ratio in the air after spraying with the selected products and perform these experiments,
- design a human pre-exposure study to determine dose-response relationships and conduct this study.

This master thesis will contribute to outline which cleaning sprays are used among the large work force of cleaning workers in Sweden. The project will also contribute to the knowledge of size distributions, airborne mass fractions and source strengths for different products. The conclusions from this thesis will form the basis for the design of human exposure studies with regard to, foremost, ethical exposure conditions and in the end hopefully result in recommendations and guidelines for use of cleaning sprays.

2. Background and theory

2.1 Aerosol definitions

An aerosol is an assembly of liquid or solid particles suspended in a gaseous medium long enough to be observed or measured. Aerosol particles are generally in the size range of 0.001 to 100 µm. If liquid droplets are formed by mechanical or electrostatic breakup of a liquid it is called spray and these aerosols are usually spherical. Aerosol generated from spraying can also be called mist or fog (Baron, 2005).

2.2 Particle size

In aerosol science the term *equivalent diameter* is often used and refers to the diameter of a sphere having the same value of a specific physical property as the particle being measured, which can be irregular in shape. *Aerodynamic diameter*, which is one of the equivalent diameters, is the diameter of a standard-density (1000 kg/m^3) sphere having the same *gravitational settling velocity* as the particle being measured. The gravitational settling velocity, or also referred to as *terminal settling velocity*, is given by:

$$V_{TS} = \frac{\rho_p d_p^2 g C_C}{18\eta} \tag{2.1}$$

where ρ_p is the particle density, $d_p$is the physical particle diameter, g is the gravitational acceleration and η is the viscosity of air. C_C is the *Cunningham slip correction factor* and is introduced due to that the suspending gas is not a continuous fluid, but consists of discrete molecules. The Cunningham slip correction factor is dependent on the particle diameter, but can be approximated with 1 for particles larger than about 1 µm, since particles of these sizes do see the suspending gas as a continuum. For a spherical, liquid droplet larger than 1 µm and with a density of 1000 kg/m^3 the aerodynamic diameter thereby equals the physical particle diameter (Baron, 2005).

2.3 Deposition mechanisms

Another important term in aerosol science is deposition, which describes the process when aerosol particles stop being airborne. Deposition is particle size dependent, but can also depend on for example surface area availability and airflows. There are six important deposition mechanisms; diffusion, gravitational settling (sedimentation), inertial impaction, interception, electrostatic attraction and thermophoresis. Different particle collection methods rely on different deposition mechanisms, but deposition can also cause unwanted losses in measuring devices and these losses have to be accounted for to get an accurate interpretation of the data (Hinds, 1999).

2.3.1 Diffusion

Diffusion of aerosol particles is the net transport of these particles in a gradient, from a region of higher concentration to a region of lower concentration (diffusion can also occur in the absence of a gradient), due to the random bombardment of gas molecules against the particles. Diffusion is the primary transport and deposition mechanism for particles less than 0.1 µm in diameter (Hinds, 1999).

2.3.2 Gravitational settling

When a particle is released in air it quickly reaches its terminal settling velocity, which is a condition of constant velocity, i.e. the drag force of the air on the particle is exactly equal and opposite to the force of gravity. As can be seen in equation (2.1) the terminal settling velocity rapidly increases with particle size and is an important deposition mechanism for particles larger than 1 µm. When sampling particles in this size range through a circular tube the deposition loss due to settling can be calculated by:

$$Settling\ loss = \frac{2}{\pi}\left(2k_1k_2 - k_1^{1/3}k_2 + arcsin\left(k_1^{1/3}\right)\right) \tag{2.2}$$

where

$$k_1 = \left(\frac{3LV_{TS}}{4D_SU}\right)\cos\theta \qquad k_2 = \left(1 - k_1^{2/3}\right)^{1/2} \tag{2.3}$$

and L is the tube length, D_S is the sampling tube diameter, U is the velocity in the sampling tube, θ is the inclination of the tube from the horizontal plane and $arcsin\theta$ is in radians (Hinds, 1999).

2.3.3 Inertial impaction

Inertial impaction occurs when a particle, because of its inertia (the tendency to keep moving in a straight line at constant velocity), is unable to quickly enough adjust to abruptly changing streamlines of the air and due to this adheres to a surface. Impaction is an important deposition mechanism for large particles and for particles with higher velocities. Sampling tube losses due to inertial impaction (called bend losses) are important to consider when sampling large particles through tubes with sharp angles (Hinds, 1999).

2.3.4 Interception

A particle that follows a gas streamline and happen to come within one particle radius from a surface can be deposited on the surface through interception. Interception is mostly important for particles in the size range of 0.1 µm to 1 µm and is a deposition mechanism especially important for fibers (Hinds, 1999).

2.3.5 Electrostatic attraction

Electrostatic attraction as a deposition mechanism can be important if the particles have been charged in some quantifiable way or are present in an electrical field, but are often neglected. Tube losses due to electrostatic attraction can be avoided by using for example Tygon sampling tubes (Hinds, 1999).

2.3.6 Thermophoresis

When a temperature gradient is established in a gas, an aerosol particle in that gas experience a force in the direction of decreasing temperature. The movement of the particle that results from this force is called thermophoresis. Thermophoresis as a deposition mechanism works for a warm flow of air in proximity to a cold surface, which will result in particle deposition onto the surface. This due to a greater transfer of momentum to the particle from the gas molecules on the warmer side of the particle than on the cold side (Hinds, 1999).

2.4 Condensation and evaporation

Condensation is the most important mass-transfer process between the gas phase and the particulate phase, which is a method of formation and growth of aerosol particles. It usually requires a supersaturated vapor and is initiated by the presence of small particles (nuclei) that serve as sites for particle formation. The reverse of growth by condensation is the process of evaporation, which means that more molecules leave the particles surface than arrive. When the partial pressure of a vapor equals its saturation vapor pressure there is mass equilibrium at the surface and evaporation from the surface just equals the condensation on that surface. The ratio between the partial pressure of a vapor and the saturation vapor pressure is called the saturation ratio. When this ratio (times 100) is applied to water vapor it is called relative humidity (RH) and the condensation/evaporation process is highly dependent on RH.

The rate of evaporation (the rate of particle size change with time) is controlled by the rate at which vapor can diffuse away from the droplet. More volatile liquids, such as alcohols, will have a shorter drying time (the time required for a droplet to evaporate completely) than for example water. For a 10 µm alcohol droplet the drying time is 0.03 seconds while it is 0.08 seconds for a 10 µm water droplet. Since droplets often are formed from a nucleus they will dry to the diameter of their original nucleus (Hinds, 1999).

2.5 Optical properties

The interaction of aerosol particles with light forms the basis for an important class of instruments used for measuring aerosol particle size and concentration by analyzing the scattering and light absorption from aerosol particles. Instruments using optical methods have the advantage of being extremely sensitive and nearly instantaneous, and does not require any physical contact with the particles. When an aerosol particle scatters light, the angle at which the scattered light is detected together with the intensity, the distance to the particle and the refractive index can be used to calculate the particle diameter (Hinds, 1999).

2.6 Air exchange rate (AER)

The air exchange rate (AER) is defined as airflow through a given space divided by its volume (as described by Wierzbicka, 2008). It is usually given in the unit h^{-1}, which means that it provides a measure of how many times per hour the air volume is replaced in the specific space. However for this condition to be valid, the air has to be perfectly mixed. The following equation is used to calculate the AER:

$$AER = \frac{Q \cdot 60}{V} \tag{2.4}$$

where Q is the air flow rate (m^3/min) and V is the volume (m^3) and AER is given in h^{-1}. A low AER will result in longer air residence time, allowing for more aerosol dynamics (e.g. coagulation) to take place.

2.7 Airborne mass fraction

The airborne mass fraction (Amf) is a measure of how much of the mass that remains airborne after aerosol emission from a specific source. When this definition is applied to a spray the following equation can be derived:

$$Amf\ (\%) = \frac{total\ mass\ remaining\ airborne}{total\ mass\ sprayed\ out} \cdot 100 \tag{2.5}$$

Equation (2.5) can be rewritten as the following to better understand how to measure the airborne mass fraction:

$$Amf(\%) = \frac{total\ mass\ sprayed\ out - total\ mass\ deposited\ on\ surface}{total\ mass\ sprayed\ out} \tag{2.6}$$

2.8 Particle concentration changes

To be able to accurately calculate particle concentration changes during experiments some initial conditions have to be met. One vital condition is to have a well-mixed experimental volume with controlled ventilation. In a well-mixed volume a mass conservation relationship can be applied according to the following equation (Koutrakis, 1991 modified by Pagels, 2009):

$$\frac{dC(t)}{dt} = aC_{inc.} + \frac{\dot{m}}{V} - (a+k)C(t) \tag{2.7}$$

where $C(t)$ is the mass concentration in the experimental volume, $C_{inc.}$ is the concentration in the incoming air, a is the air exchange rate (AER) (s^{-1}), k is the sum of other losses (s^{-1}), usually particle size dependent (as described in section 2.3), $\dot{m}$ is the mass emission factor (kg s^{-1}), also called source strength, and V is the volume (m^3). Assuming that the initial concentration is zero and that $\dot{m}$ is constant over time, equation (2.7) has the following solution:

$$C(t) = \frac{\dot{m}}{V(a+k)} \cdot \left(1 - e^{-(a+k)\cdot t}\right) \tag{2.8}$$

The source strength describes how much mass a specific particle source emits per time unit. Equation (2.8) describes how the concentration increases in an experimental volume over time with a constant particle source. The concentration decay in an experimental volume can be described with the following equation (Drivas, 1996):

$$C(t) = C_0 \cdot e^{-(a+k)t} \tag{2.9}$$

where C_0 is the initial background concentration. If this equation is made logarithmic a linear relationship is found:

$$\ln\big(C(t)\big) = -(a+k)t + \ln(C_0) \tag{2.10}$$

This relationship can be used to find the deposition losses $(a+k)$ in the experimental volume during the conditions for which the concentration is measured.

2.9 Equipment

2.9.1 Scanning Mobility Particle Sizer – SMPS

A Scanning Mobility Particle Sizer (SMPS, model 3934, TSI Inc.), consisting of a DMA (Differential Mobility Analyzer) and a CPC (Condensation Particle Counter), was used to measure the particle concentration and size distribution during the initial tests in the exposure chamber. The SMPS can measure size distributions from 0.01 to 1 µm.

2.9.2 Aerodynamic Particle Sizer – APS

An Aerodynamic Particle Sizer (APS, model 3321, TSI Inc.) was used to measure the particle concentration and size distribution during the initial tests in the exposure chamber as well as the measurements in the experimental volume. The APS uses a time-of-flight particle sizing technology and measures both aerodynamic diameter and light-scattering intensity. The technology involves measuring the acceleration of aerosol particles in response to the accelerated flow of the sample through a nozzle and the aerodynamic diameter of a particle determines its rate of acceleration. When the particle exits the nozzle the time-of-flight between two laser beams is recorded and converted to aerodynamic diameter with the help of a calibration curve. The APS can measure size distributions for particles with aerodynamic diameters from 0.5 to 20 µm. Figure 2.1 shows the schematics of the APS measuring system and Table 2.1 shows all the data channels (aerodynamic diameter) for which the APS stores the data.

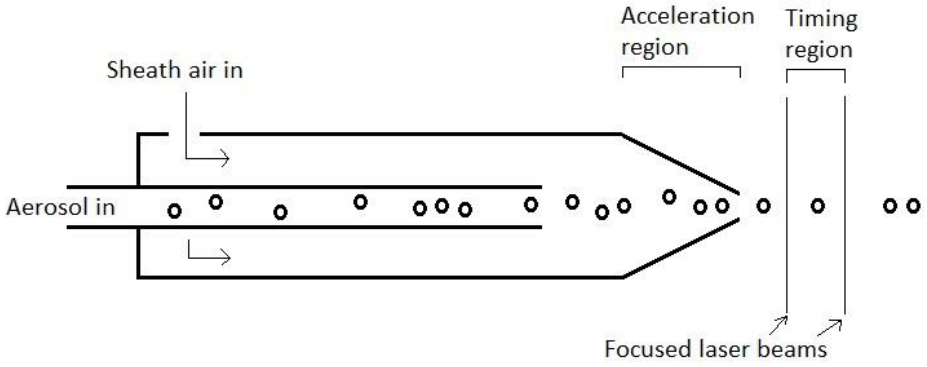

Figure 2.1 Schematics of the APS measuring system.

Table 2.1 The APS channels.

<0.523 µm	1.286 µm	3.278 µm	8.354 µm
0.542 µm	1.382 µm	3.523 µm	8.977 µm
0.583 µm	1.486 µm	3.786 µm	9.647 µm
0.626 µm	1.596 µm	4.068 µm	10.37 µm
0.673 µm	1.715 µm	4.371 µm	11.14 µm
0.723 µm	1.843 µm	4.698 µm	11.97 µm
0.777 µm	1.981 µm	5.048 µm	12.86 µm
0.835 µm	2.129 µm	5.425 µm	13.82 µm
0.898 µm	2.288 µm	5.829 µm	14.86 µm
0.965 µm	2.458 µm	6.264 µm	15.96 µm
1.037 µm	2.642 µm	6.732 µm	17.15 µm
1.114 µm	2.839 µm	7.234 µm	18.43 µm
1.197 µm	3.051 µm	7.774 µm	19.81 µm

2.9.3 DustTrak Aerosol Monitor

A DustTrak Aerosol Monitor (DustTrak, model 8520, TSI Inc.) was used to measure the particle mass concentration during the initial tests in the exposure chamber as well as the preliminary characterization of the experimental volume. DustTrak uses a light-scattering technology (described in section 2.5) to determine mass concentration in real-time and can detect particles in the size range of 0.1 to about 10 μm.

2.9.4 Palas generator

A powder particle generator (Palas, model BEG 1000, Palas GmbH) was used to generate spherical, solid particles that were used to measure the characteristics of the experimental volume (described in section 3.4.2). The particles are generated from glass powder which is poured into a reservoir on the generator. At the bottom of the reservoir a stirrer is placed to ensure uniform loading to the nozzle. The mass flow can be continuously and reproducibly adjusted to ensure dosing constancy.

2.9.5 Malvern Mastersizer

A Malvern Mastersizer X standard bench (Malvern, model MAM 5000, Malvern Instruments Ltd) was used to measure the size range of the initial spray droplet diameter (just when they exit the spray bottle nozzle). These measurements were used to validate the results from the APS. The Malvern Mastersizer uses a light-scattering technology (described in section 2.5) to measure the size of particles. It consists of a laser transmitter, a sample area and a receiver. At the end of the sample area a lens, called range lens (number 3 in Figure 2.2), is placed to collect the scattered laser light and focus it onto the detector electronics in the receiver. Figure 2.2 shows the schematics of the sample area into which the products are sprayed.

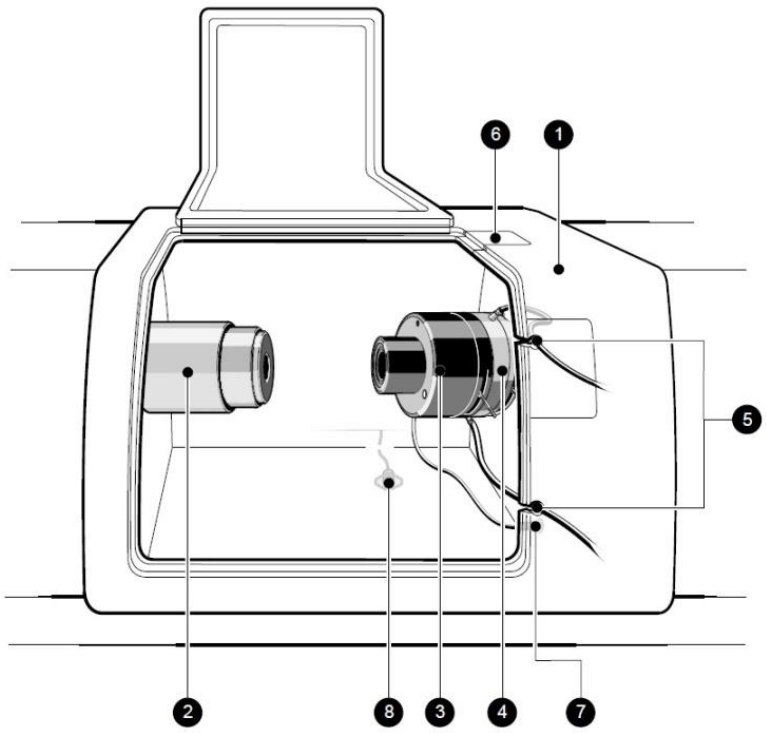

Figure 2.2 Schematics of the sample area of the Malvern Mastersizer (Malvern Instruments Ltd).

Different analysis models can be chosen to present the data from the Malvern Mastersizer. The polydisperse model is a model that does not assume anything about the shape of the result graph, in comparison to for example mono- or multimodal models that assumes there will be one or more peaks in the result graph. The size distribution derived by this technique is volume based and uses the method known as *equivalent spheres*, meaning that the volume of the particle measured is used to calculate the diameter of a sphere with equivalent volume. The data from the Malvern Mastersizer is presented in a variety of ways and one of these are as the *mass median diameter (MMD)*, which is the particle diameter at which 50 % of the sample (by mass) is smaller and 50 % is larger in size, that is the most commonly occurring particle diameter. This value is denoted as D(v, 0.5) in the data print out and is derived from a cumulative curve (described in section 4.2.4).

3. Methods

3.1 Product identification and selection

A phone based survey with 20 Swedish cleaning companies was conducted for the purpose of identifying which cleaning sprays are most frequently used. A questionnaire (Appendix A) was designed, for the purpose of finding out if the companies use spray products and if so on what surfaces. Specific products used for the different surfaces were also identified. From these phone-interviews a qualified selection of products were chosen for characterization.

3.2 Exposure chamber

A human exposure chamber was used for the primary tests and the pre-exposure study. It is a 21.6 m^3 stainless steel room with one 0.8 m^2 glass window. An antechamber, 3.1 m^3 in size, with air tight doors (one facing the exposure room and the other facing the surrounding laboratory) is used to enter the exposure room. A well-controlled ventilation system only allows air to enter and leave the chamber in a properly-monitored manner and the air supplied to the antechamber is exhaust air from the exposure room. This to reduce the possibility of contamination of the air in the exposure room when entering and leaving. The air to the chamber is supplied through a separate custom-built conditioning system where temperature, RH and air flow can be regulated. As well as being filtered inside the conditioning system, the air supplied to the chamber is also filtered through an activated carbon filter, which removes gases, and an ultra-low penetration air (ULPA) filter, which removes 99.999 % of particles 0.12 µm in size or larger, before entering at roof level. The exposure chamber exhaust outlet is situated in the diagonally opposite corner of the air inlet, at a height of 0.8 m from the chamber floor. A variable exhaust fan is used to regulate the exhaust flow. Due to this construction a desired slight over-pressure or under-pressure can be maintained. An express fan can also be switched on to quickly empty the chamber of aerosols, in this case the air is supplied from the surrounding room, but passes through a filter with pelleted active carbon as well as through a high efficiency particulate arresting (HEPA) filter before entering the chamber at an AER of about 15 h^{-1}. The HEPA filter removes 99.97 % of 0.3 µm sized particles (the particle size which is the most difficult to filter) and removes an even higher degree of particles larger and smaller in size (Isaxon, 2013). Figure 3.1 shows the schematics of the exposure chamber.

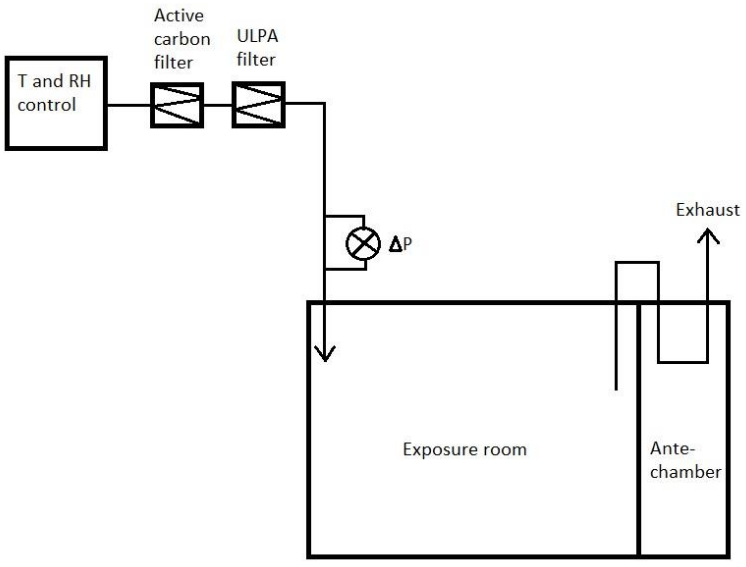

Figure 3.1 Schematics of the exposure chamber.

3.3 Experimental volume

Based on the conclusions (see section 5.2) from the initial tests in the exposure chamber a smaller experimental volume was chosen for the characterization of products during the work with this thesis. The experimental volume is a 1.2 m^3 stainless steel chamber with one 1.1 m^2 glass door. The glass door is provided with one attached glove and one sealable (with duct tape) opening for measurement equipment. Air from the conditioning system is introduced in the bottom of the experimental volume and the exhaust outlet is placed on the top, providing a steady, controlled flow of clean air through the experimental volume. In connection to the air inlet a rotameter is placed to monitor the air flow. Figure 3.2 shows the schematics of the experimental volume.

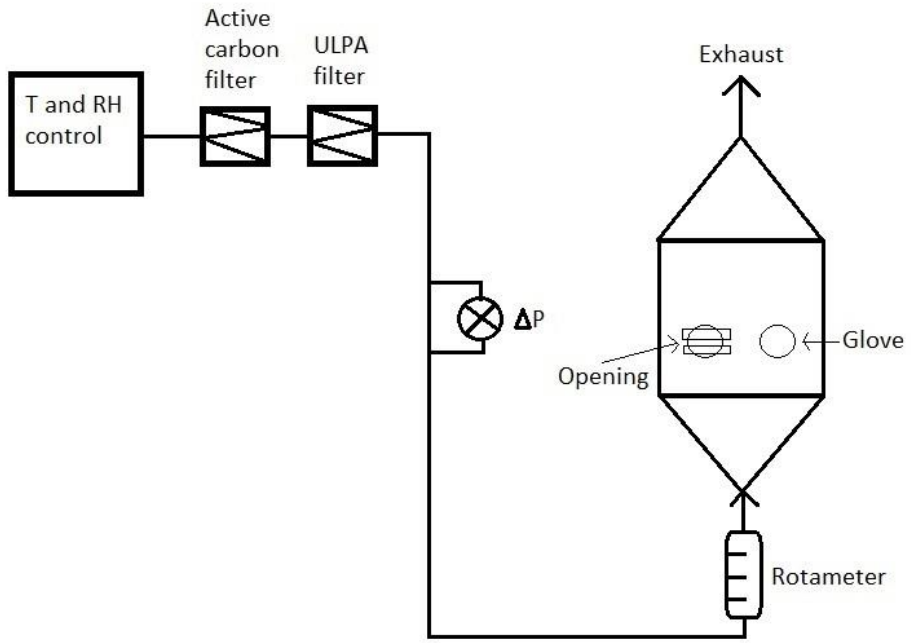

Figure 3.2 Schematics of the experimental volume.

3.4 Laboratory work

During all the laboratory work the temperature and the RH were monitored with a SwemaAir 300 monitor. The AER was monitored with the rotameter (described in section 3.4.2.1). During the characterization measurements in the experimental volume a temperature of 20°C (± 0.3°C), a RH of 38 % (± 6 %) and an AER of 0.7 h^{-1} was upheld. Tygon sampling tubes were used for all the measurements.

3.4.1 Initial test measurements

A few particle concentration and size distribution measurements were performed in the exposure chamber with a small selection of test spray products. SMPS, APS and DustTrak were used to do these measurements and the results provided information about the relevance of the different measurement instruments for this particular aerosol.

3.4.2 Characterization of experimental volume

Before the experimental volume could be used for measurements it was characterized in terms of AER, concentration uniformity and deposition losses.

3.4.2.1 Rotameter calibration

To be able to determine the AER in the experimental volume, the rotameter attached to the inlet flow was calibrated. The inlet tube was detached from the experimental volume and a flowmeter was connected at the end of the tube. Different valve settings were chosen and the value of the rotameter was compared to the measured air flow from the flowmeter. A calibration curve was then generated for calculation of the AER.

3.4.2.2 Concentration uniformity

To assure that the particle concentration was uniform in the whole volume a few different concentration measurements were performed. A uniform air flow through the experimental volume was preliminary (visually) verified by the use of smoke ampoules. Then the Palas generator was used to generate solid glass particles, which were introduced into the volume through a tube through the sealable opening, in a way similar to that with which the sprays would be used. An air pressure of 1 bar was used and a Y-connection was attached to the outlet providing an air flow of 4.5 l/min into the experimental volume. A small fan was also placed in one of the corners and set to a slow mode with the help of a dimmer. Figure 3.3 shows a picture of the experimental volume and the placement of the fan.

Figure 3.3 The experimental volume used for the measurements and the placement of the fan.

The particle mass concentration was measured with the DustTrak in seven different points in the volume and compared with the value in the center (c). A tube connected to the DustTrak was inserted through the opening to perform these measurements.

To be able to sample and collect size distributed data the Palas generator was then used together with the APS. To examine the effect of the fan it was turned off during these measurements. Due to the different distances from the opening to the measuring points, two different tubes were used for the measurements. The different points that were measured in the volume are shown in Figure 3.4 and the order of which they were measured in and with which tube are shown in Table 3.1.

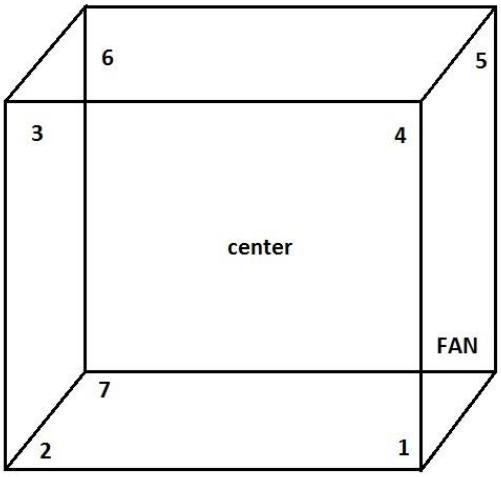

Figure 3.4 The different points in which the particle concentration was measured.

Table 3.1 The order in which the points were measured and with which tube.

Tube	Order of measurement
Short tube	center
	1
	2
	3
	center
Long tube	center
	4
	5
	6
	7
	center

3.4.2.3 Deposition losses

The deposition losses in the experimental volume were determined to be able to correctly determine the source strength for the selected products. Again, the Palas generator was used to generate particles which were introduced into the volume in the same way as during the concentration measurements. When the generator had been running for about three minutes it was turned off and the concentration decay was measured.

First the DustTrak was used to measure the concentration while the fan was on, but due to the desire to obtained size distributed data, as previously stated, the APS was used for the remaining measurements. A test spray product was used with the fan on to examine if the spray concentration decayed in a similar way as the solid particles from the preliminary test with the DustTrak. Finally the Palas generator was used together with the APS to measure the decay with and without the fan on.

3.4.3 Airborne mass fraction

The idea for the airborne mass fraction measurements was to spray with the product against a wall, to mimic how a cleaning product generally is used, and measure the total weight of the mass that left the bottle during spraying as well as measure the weight of the mass that was deposited on the wall, thereby being able to determine how much mass remained airborne, the airborne mass fraction.

To be able to measure the mass deposited on the wall the droplets had to be collected in a way that makes it possible to weigh. The simplest idea was to use paper and tape in on the wall, at which the spraying was done. A few different paper-setups was tried, two different types of paper and two different number of layers of paper. Based on the results from these paper-setup-tests the chosen setup consisted of three white paper napkins unfolded on top of each other to cover an area of 40 cm x 40 cm. For easier handling the three sheets of paper were taped together in the two upper corners. To avoid evaporation during movement from the spray experiment area to the weighing area the papers were put in a plastic jar with a screw cap. Figure 3.5 shows the paper-setup used for the airborne mass fraction measurements as well as the jar used to avoid evaporation.

Figure 3.5 The paper-setup used for the airborne mass fraction measurements and the plastic jar used to avoid evaporation (in front of the scale used).

The following protocol for airborne mass fraction measurements was developed and the experiments were performed accordingly:

Protocol for airborne mass fraction measurements

1. Weigh the spray bottle
2. Weigh the papers inside the plastic jar with the cap screwed on
3. Move the bottle and the papers (still inside the plastic jar) to the spray experiment area
4. Take two additional pieces of tape and tape the papers to the wall
5. Spray once at the papers on a distance of about 30 cm (according to the user instructions)
6. Put the papers in the jar and screw on the cap
7. Weigh the spray bottle
8. Weigh the jar with the papers inside
9. Calculate the airborne mass fraction according to section 3.5.2

The paper-setup-test and initial test measurements of airborne mass fractions were performed in the exposure chamber but, as mentioned above, the characterizations of the selected products were performed in the experimental volume. Based on the results (see section 4.2.1.2 and 4.2.1.3) from the concentration and decay measurements of the experimental volume the fan was removed for the airborne mass fraction measurements as well as for the source strength measurements.

3.4.4 Source strength

The source strength measurements were performed in a similar way as the concentration decay measurements, Figure 3.6 shows a picture of the setup for these measurements.

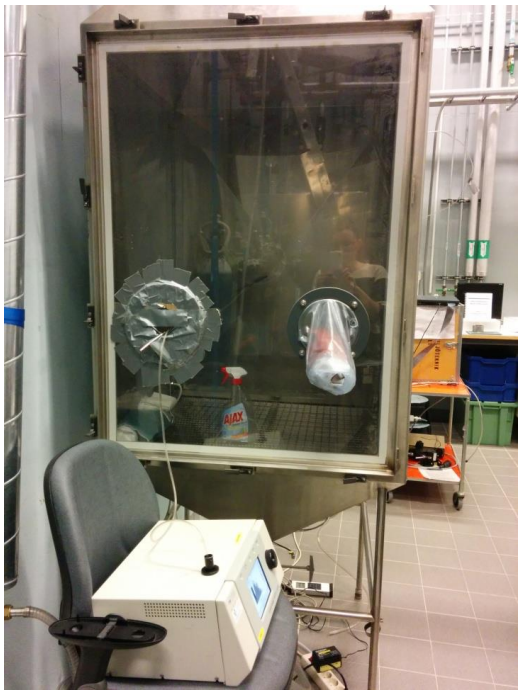

Figure 3.6 The source strength measurements setup.

The following protocol for source strength measurements was developed and the experiments were performed accordingly:

Protocol for source strength measurements

1. Weigh the spray bottle
2. Place the spray bottle in the experimental volume
3. Place the APS outside and mount the sampling tube through the opening so it measures in the center of the volume
4. Choose an appropriate sampling time (e.g. 2 seconds)
5. Turn on the APS and let it measure the background for one or two minutes (depending on the sampling time)
6. Spray with a fixed spray rate (e.g. 1 spray/second) against the wall for one or two minutes (depending on the product)
7. Stop spraying and let the APS measure the concentration decay for about 20 minutes
8. Stop the measurement
9. Weigh the spray bottle
10. Calculate the source strength according to section 3.5.3

3.4.5 Validation of APS data

To validate the data obtained from the APS during the source strength measurements, the initial spray droplet diameter was determined with the Malvern Mastersizer (described in section 3.5.4). The selected products were measured by spraying into the sample area, while making sure the spray stream crossed the laser beam (called obscuration, which is the fraction of light from the analyzer beam that is blocked by the sample). An obscuration of 5-30 % was upheld since this is the ideal range (5-10 % usable). The scattering data was then processed by the Malvern Mastersizer software and the polydisperse model was chosen to analyze the data. For the measurements conducted during the work with this thesis a 300 mm range lens was used to provide data in the particle size range of 1.2 to 600 µm, which is recommended for spray measurements.

3.5 Data analysis

3.5.1 Deposition losses

Since the deposition losses are size dependent the APS data was analyzed for eight different particle sizes which were: 0.6, 1, 2, 3, 4, 5, 6 and 7 µm. A few different APS channels were averaged for each of these sizes (e.g. 2.839 µm, 3.051 µm and 3.278 µm were averaged to get the 3 µm value). Equation (2.10) describes the linear relationship that is found when the equation for the concentration decay in the experimental volume is made logarithmic. The averaged values were hence plotted over time on a logarithmic scale. A linear regression was made to find the coefficient of slope for each particle size. The eight coefficients were plotted, and a fitted equation was found which described the deposition losses' $(a + k)$ size dependence.

3.5.2 Airborne mass fraction

The airborne mass fraction measurements were performed three times for each of the selected products. The airborne mass fraction was then calculated according to the following equation based on equation (2.6):

$$Amf = \frac{(B_b - B_a) - (P_a - P_b)}{B_b - B_a} \cdot 100 \tag{3.1}$$

where Amf is the airborne mass fraction (%), B_b is the bottle weight before spraying, B_a is the bottle weight after spraying, P_b is the papers weight before spraying and P_a is the papers weight after spraying. From the P_a value the weight of the additional pieces of tape used was subtracted, a standard value of 0.033 g was used for this adjustment. The standard deviation (SD) and the relative standard deviation (rel. SD) were also calculated for the airborne mass fractions.

3.5.3 Source strength

An excel-simulation program was used to calculate the source strength according to equation (2.8). The source strength was calculated for a representative selection of the APS channel sizes for which the different deposition losses obtained were used. The channels used for calculating the different source strengths are shown in Table 3.2.

Table 3.2 The APS channels used for source strength calculation.

APS channel	0.626 µm	0.777 µm	0.898 µm	1.037 µm	1.286 µm	1.486 µm	1.715 µm	1.981 µm	2.288 µm	2.642 µm	3.051 µm	3.523 µm	4.068 µm

Due to the sampling tube setup the calculated source strength values were then adjusted for tube losses. The tube losses were approximated to only consist of losses due to gravitational settling (bend losses were neglected since there were no sharp angles in the sampling tube setup) and these losses were calculated for a 0.5 m long tube in an angle of 40° from the horizontal plane and for a 0.4 m long tube parallel to the horizontal plane, both with an inner diameter of 3 mm. The tube losses were calculated with the help of another excel-calculation program called Aerocalc (created by Paul Baron in 2001) based on equation (2.2). The adjusted source strength values were then plotted and a cubic curve was fitted to obtain an equation from which the source strength values could be calculated for all the APS channel sizes. To obtain the total source strength value for the particles ($\dot{m}(particles)$) the channel values from the lowest channel size (with a positive value) to the channel size corresponding to the APS MMD value (seen in Table 4.3) were summed up and then multiplied with 2. This since a normal distributed curve was assumed, in the same way as for the size distribution.

The total source strength for the bottle was calculated from the difference in bottle weight before and after spraying and then divided with the time during which the mass was sprayed out. The following equation can be used to calculate the total source strength:

$$\dot{m}(total_{bottle}) = \frac{B_b - B_a}{t} \tag{3.2}$$

where t is the time during which the mass was sprayed out. This total source strength for the bottle consists of the amount deposited on the wall ($\dot{m}\left(surface_{mass\ fraction}\right)$) and the amount emitted into the air ($\dot{m}(air)$). $\dot{m}(air)$, in turn, consist of the sum of particles and gas, which is regulated by the evaporation/condensation process (described in section 2.4). A mass balance equation to describe this can be written as:

$$\dot{m}(total_{bottle}) = \dot{m}\left(surface_{mass\ fraction}\right) + \dot{m}(particles) + \dot{m}(gas) \tag{3.3}$$

From this relationship the particle/gas ratio can be determined.

3.5.4 Validation of APS data

From the APS data the ratio of $\dot{m}(particles)$ and $\dot{m}(total)$ can be found. This percentage states how much of the mass sprayed out of the bottle that becomes airborne particles. This can be compared to the particle volume (and essentially diameter) ratio from the dried particles measured by the APS and the particles directly out of the nozzle (from the Malvern Mastersizer). Since the volume of a sphere is given by the equation:

$$V_{sphere} = \frac{\pi}{6} \cdot d^3 \tag{3.4}$$

the particle diameter ratio (R_d) is given by:

$$R_d = \frac{V_{APS}}{V_{Malvern}} = \frac{d_{APS}^3}{d_{Malvern}^3} \tag{3.5}$$

To be able to compare the two particle diameters the MMD needs to be estimated from the APS data. This was done by creating a cumulative curve from the size distribution concentrations and then reading the diameter value corresponding to 50 %.

3.6 Pre-exposure dose-response study

After all the product characterization measurements one of the products were chosen for a pre-human exposure study. For this study eight human volunteer test subjects were exposed to five different doses during one day. In total, this study was conducted over two days with four subjects being exposed each day. This pre-study did only focus on acute symptoms in the upper airways and eyes (no ergonomic symptoms were examined).

For this study a few different questionnaires were developed in collaboration with physicians. One concerning the general health (Appendix B), with questions regarding eye health and allergies. Three symptom questionnaires were also designed based on previous exposure study questionnaires, and a small pilot study conducted a few weeks before the pre-exposure study, for the purpose of determining which symptoms that would be interesting to include and which doses to test. The three questionnaires were "Before exposure" (Appendix C), "During exposure" (Appendix D) and "After exposure" (Appendix E) and the symptom questions included different nose, eye and throat symptoms and symptoms connected to the smell.

In addition to the questionnaires, two different, non-invasive, medical examinations were done. The first one was a measure of the Peak Nasal Inspiratory Flow (PNIF) to assess the patency of the nose. A PNIF meter was used, whose applications include diagnosis of nasal obstruction and the assessment of response to nasal provocation. The PNIF meter consists of a tube calibrated directly in liters per minute including a low inertia indicator ring, whose position after inspiration clearly indicates the maximum flow achieved. It is used together with a reusable mask (GM instruments). Figure 3.7 shows the PNIF meter used.

Figure 3.7 The PNIF meter used during the pre-exposure study.

The other examination was done to asses the Break-Up Time (BUT) of the tear film and a Tearscope was used for this measurement. The Tearscope is an ocular microscope that uses a technique based on a grid of equidistant circles of light that are blurred by tear film break up (Moen, 2011). Figure 3.8 shows the Tearscope used and the grid of light.

Figure 3.8 The Tearscope used during the pre-exposure study.

The subjects were exposed to four different spray doses and one "cloth and bucket"-dose. Four equal spray bottles with two different concentrations were masked and marked with A, B, C and D. Bottle A and D contained the cleaning product and bottle B and C contained tap water, in an attempt not to make it apparent for the subject which dose they were currently being exposed to. The four different spray doses were achieved by letting the subject spray the window in the exposure chamber with different series of bottles and different number of sprays with each bottle. Table 3.3 shows how the different doses were applied. This resulted in a twentyfold increase in dose from the lowest to the highest dose.

Table 3.3 Spray-dose layout.

Spray dose	**Number of sprays with product**	**Bottle: number of sprays**					
1 (lowest)	3	A: 3	B: 3	C: 3	-	-	-
2	9	A: 3	A: 3	D: 3	-	-	-
3	30	A: 10	A: 10	B: 10	B: 10	C: 10	D: 10
4 (highest)	60	A: 10	A: 10	D: 10	D: 10	A: 10	D: 10

After each bottle had been used (either by three sprays or by ten) the window was wiped dry with paper cloths. The "cloth and bucket"-dose was applied using a bucket filled with the cleaning product and a textile cloth which was dipped in the bucket, squeezed and then used to wet wipe the window. After the wet wipe, the window was wiped dry with paper cloths as before. This procedure was done six times as a comparison to the highest spray dose, where the window was cleaned six times.

A protocol for the exposures were developed and the experiments were performed accordingly:

Protocol for pre-exposure study

1. Inform the subject of how the exposure will be done and which examinations that will be performed
2. Inform the subject that they can stop the exposure-day whenever they want, without having to state a reason
3. Let the subjects fill out the "General health" questionnaire and do a short physical examination
4. Let the subject sign a consent form and let the physician approve the participation
5. Let the subject fill out the "Before exposure" questionnaire
6. Let the subject perform a "PNIF before" measurement
7. Let the subject perform a "BUT reference" measurement
8. Let the subject enter the exposure chamber
9. Give instructions on how to perform the exposure (which bottle to use and the number of sprays)
10. Let the subject spray the window from a distance of about 30 cm
11. Start a timer for 10 minutes when the first spray is applied
12. Start a new timer for 2 minutes when the spray series is completed
13. Let the subject stand at the same place in front of the window during the whole exposure
14. When the 2 minute timer is up, let the subject fill out the "During exposure" questionnaire
15. When the 10 minute timer is up, let the subject exit the chamber and set the timer to a new 10 minutes
16. Let the subject perform a "BUT after" measurement

17. Let the subject perform a “PNIF after” measurement
18. When the 10 minute timer is up, let the subject fill out the “After exposure” questionnaire

Step 1-4 and 7 were only performed before the first exposure. The PNIF measurements were performed three times at each occasion and the BUT measurements were performed six times (three times on each eye) after each exposure (as well as at the first reference measurement). During the exposures an AER of 0.5 h^{-1} was upheld through the exposure chamber and a slight over-pressure was maintained to prevent particles from the surrounding room to leak into the chamber. The temperature and the RH were also monitored and a temperature of about 24.0°C ($\pm$ 0.4°C) as well as an RH of about 27.0 % ($\pm$ 2.0 %) was upheld. Between each exposure the chamber was express ventilated to make sure all subjects started the exposure with the same aerosol free background. During the pre-exposure study, the regular exhaust flow was disconnected from the antechamber and the outer door was open for easier and quicker access to the exposure room.

An ethics review has to be submitted to the local ethics committee to be allowed to perform human studies. Studies were humans are being exposed to different kind of particles and during which biological samples are collected (such as blood and urine) and medical examinations are performed, are examples of human studies that requires approval from the local ethics committee. The researchers at the division of Ergonomics and Aerosol Technology have previously submitted an ethics review to the Ethical Review Board at Lund University for these kind of human exposure studies, which is still valid. Since only questionnaires and non-invasive examinations were going to be used during this human pre-exposure study no additional compliment to the ethics review had to be submitted. The following statement is therefore valid.

The study was approved by the local ethics committee according to the declarations of Helsinki and an informed consent was obtained from all subjects prior to exposure.

4. Results

4.1 Product identification and selection

The following products were chosen for characterization:

- Johnson Diversey TASKI Sani 100 free (for bathrooms)
- Johnson Diversey Sprint Glass (for windows and mirrors)
- Johnson Diversey Suma Inox D7.1 (for stains)
- Ajax Bathroom (for bathrooms)
- Ajax Crystal Clean (for windows and mirrors)
- Ajax Universal (for all surfaces)

The products from Ajax were purchased at a local supermarket, but the products from Johnson Diversey had to be obtained from a wholesaler providing cleaning products to companies. However the products available were not exactly the same as the previously selected and the Johnson Diversey products finally purchased were:

- Johnson Diversey TASKI Sani 100 free (for bathrooms)
- Johnson Diversey Sprint Glass Pur-Eco (for windows and mirrors)
- Johnson Diversey Sprint Spitfire Spray (for stains)

Johnson Diversey TASKI Sani 100 free was not delivered in a spray bottle, which is why a separate bottle was purchased and the solution was mixed according to the instructions. Figure 4.1 shows the six different products examined.

Figure 4.1 The six different products examined.

4.2 Laboratory work and data analysis

4.2.1 Characterization of experimental volume

4.2.1.1 Rotameter calibration

Figure 4.2 shows the rotameter calibration curve.

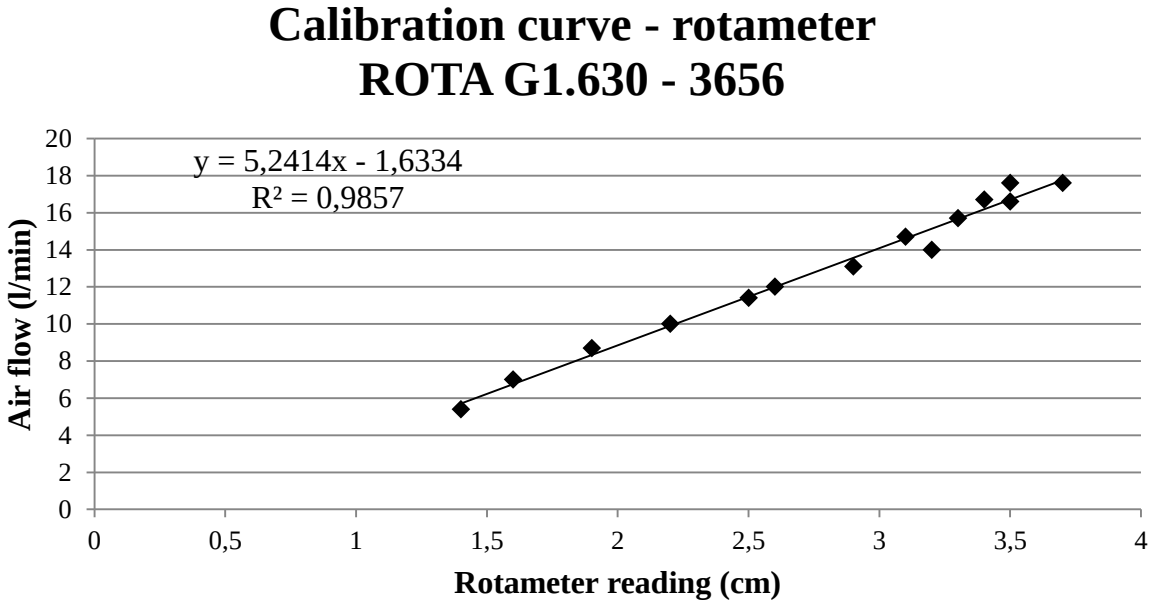

Figure 4.2 Calibration curve for the rotameter attached to the experimental volume.

The equation derived from the calibration curve is the following:

$$Q = 5.2414 \cdot h - 1.6334 \tag{4.1}$$

where Q is the air flow (l/min) and h is the rotameter reading (cm). From this equation the AER (h^{-1}) can be calculated with the following equation based on equation (2.4):

$$AER = Q \cdot \frac{60}{1000 \cdot V} \tag{4.2}$$

where Q is given in l/min and the volume (V) for the experimental volume is 1.2 m^3.

4.2.1.2 Concentration uniformity

Figure 4.3 shows the particle concentration values for the Palas generator without the fan.

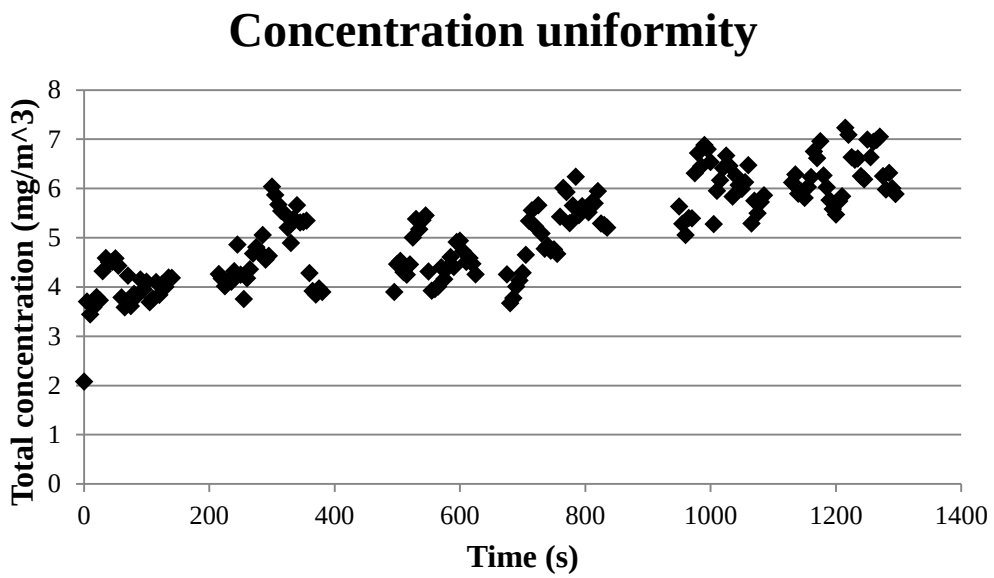

Figure 4.3 Particle concentration values for Palas generator without fan (measured with APS).

From the figure it is apparent that the concentration was relatively uniform between the different measuring points, but that the concentration in the volume increased over time. Figure 4.4 shows the mean particle concentration values normalized against the value in the center of the experimental volume.

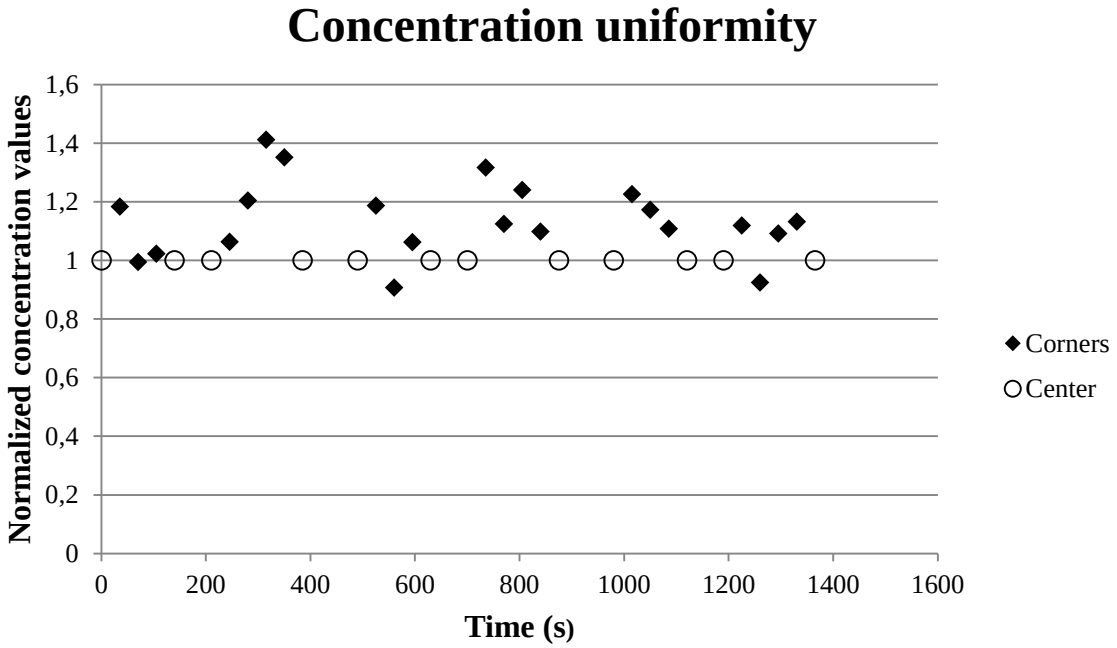

Figure 4.4 Normalized particle concentration values for Palas generator without fan (measured with APS).

The normalized particle concentration values show a relative standard deviation (variation) of 11.3 % and a variation under 20 % was considered acceptable.

4.2.1.3 Deposition losses

Figure 4.5 shows the size dependence of the deposition losses for Palas generator without fan (measured with APS).

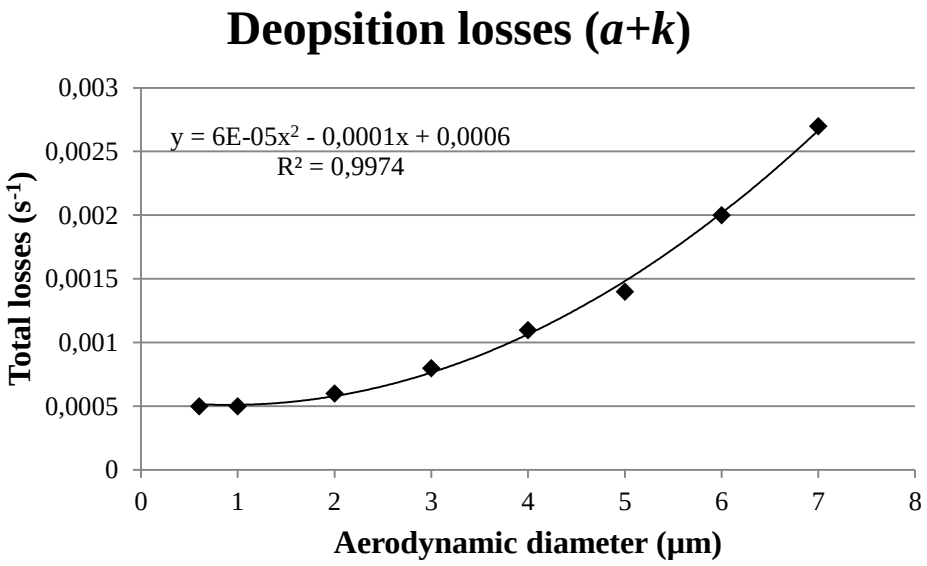

Figure 4.5 The deposition losses' (a+k) size dependence.

The equation derived from this graph is the following:

$$a + k = 6 \cdot 10^{-5} \cdot d_p^2 - 0.0001 \cdot d_p + 0.0006 \qquad (4.3)$$

where $(a + k)$ is given in s^{-1} and d_p in µm and it was used for calculating the deposition losses for the APS channel sizes chosen for the source strength calculations.

4.2.2 Airborne mass fraction

Table 4.1 shows the airborne mass fraction, the standard deviation and the relative standard deviation for six different cleaning products examined.

Table 4.1 The airborne mass fraction, standard deviation and relative standard deviation for the products examined.

Product	Amf (%)	SD (%)	Rel. SD (%)
Ajax Bathroom	7.0	1.1	15
Ajax Crystal Clean	15.7	1.6	10
Ajax Universal	4.9	0.2	4
Johnson Diversey TASKI Sani 100 free*	20.2	4.9	24
Johnson Diversey Sprint Glass Pur-Eco	9.1	1.0	11
Johnson Diversey Sprint Spitfire Spray	2.7	0.5	17

*Separate bottle was used on which the nozzle was turned 270 degrees to provide a spray stream similar to Ajax Bathroom (for comparability).

The table show higher airborne mass fractions for the window cleaning sprays (Ajax Crystal Clean and Johnson Diversey Sprint Glass Pur-Eco) compared to the sprays for stains (Johnson Diversey Sprint Spitfire Spray) and all surfaces (Ajax Universal). The non-commercial bathroom spray (Johnson Diversey TASKI Sani 100 free) showed the highest airborne mass fraction, however this product was tested with a separately purchased bottle.

4.2.3 Source strength

Table 4.2 shows the source strength values for the bottle, the surface and the particles.

Table 4.2 Source strength values for the bottle, the surface and for the particles.

Product	$\dot{m}(total_{bottle})$ **(mg s^{-1})**	$\dot{m}(surface_{mass\ fraction})$ **(mg s^{-1})**	$\dot{m}(particles)$ **(mg s^{-1})**
Ajax Bathroom	1227	1141	0.00226
Ajax Crystal Clean	342	288	0.00103
Ajax Universal	1114	1060	**
Johnson Diversey TASKI Sani 100 free*	847	676	0.01727
Johnson Diversey Sprint Glass Pur-Eco	618	562	0.00831
Johnson Diversey Sprint Spitfire Spray	1142	1111	0.00017***

*Separate bottle was used on which the nozzle was turned 270 degrees to provide a spray stream similar to Ajax Bathroom (for comparability).
**Too low concentrations were achieved and the source strength could not be simulated.
***This value was obtained from a poor fitting.

The table shows very low source strength values for the particles, meaning that almost all of the mass remaining in the air will evaporate to gas. From equation (3.3) the source strength values for the gas can be calculated as well as the particle/gas ratio and these are shown in Table 4.3.

Table 4.3 Source strength values for the gas and the particle/gas ratio.
The source strength ratios have been multiplied with 100 for comparison in percentage.

Product	$\dot{m}(gas)$ **(mg s^{-1})**	**Particle/gas ratio (%)**
Ajax Bathroom	85.99774	0.0026
Ajax Crystal Clean	53.99897	0.0019
Ajax Universal	**	**
Johnson Diversey TASKI Sani 100 free*	170.98273	0.0101
Johnson Diversey Sprint Glass Pur-Eco	55.99169	0.0148
Johnson Diversey Sprint Spitfire Spray	30.99983***	0.0005***

*Separate bottle was used on which the nozzle was turned 270 degrees to provide a spray stream similar to Ajax Bathroom (for comparability).
**Too low concentrations were achieved and the source strength could not be simulated.
***This value was obtained from a poor fitting.

The table shows that more than 99.9 % of the mass remaining airborne, for all products, will be gas.

4.2.4 Validation of APS data

The APS data was used to plot the size distribution for all the characterized products. Figure 4.6 shows a typical example of what the size distributions look like, this for Johnson Diversey Sprint Glass Pur-Eco.

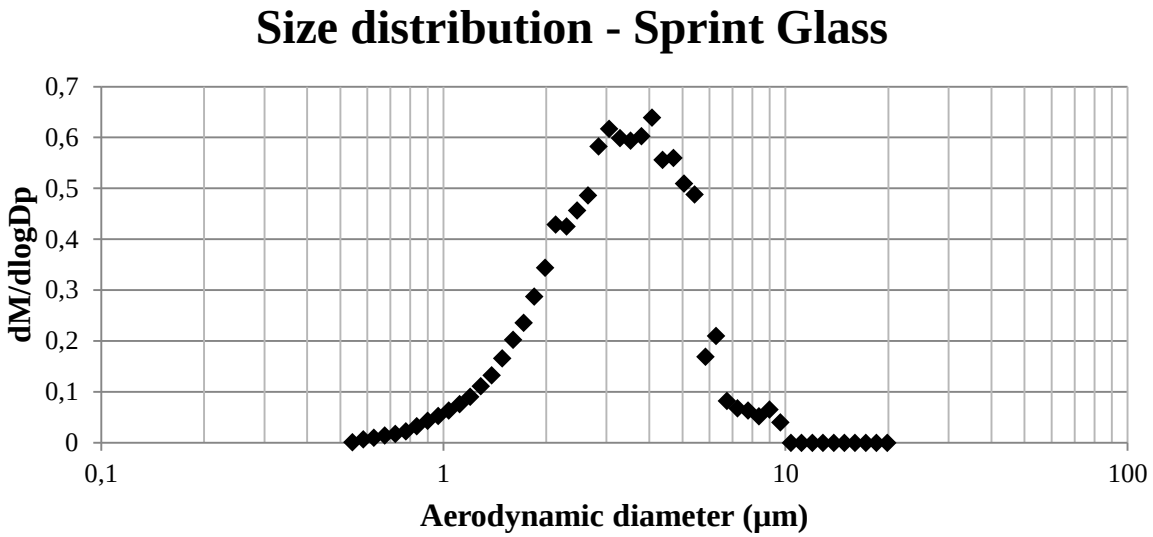

Figure 4.6 The size distribution for Johnson Diversey Sprint Glass Pur-Eco.

Each concentration value from the size distribution was then summed up with the previous value and all these sums were normalized against the total sum to create a cumulative curve. Figure 4.7 shows a typical example of what the cumulative curves look like, this for Johnson Diversey Sprint Glass Pur-Eco.

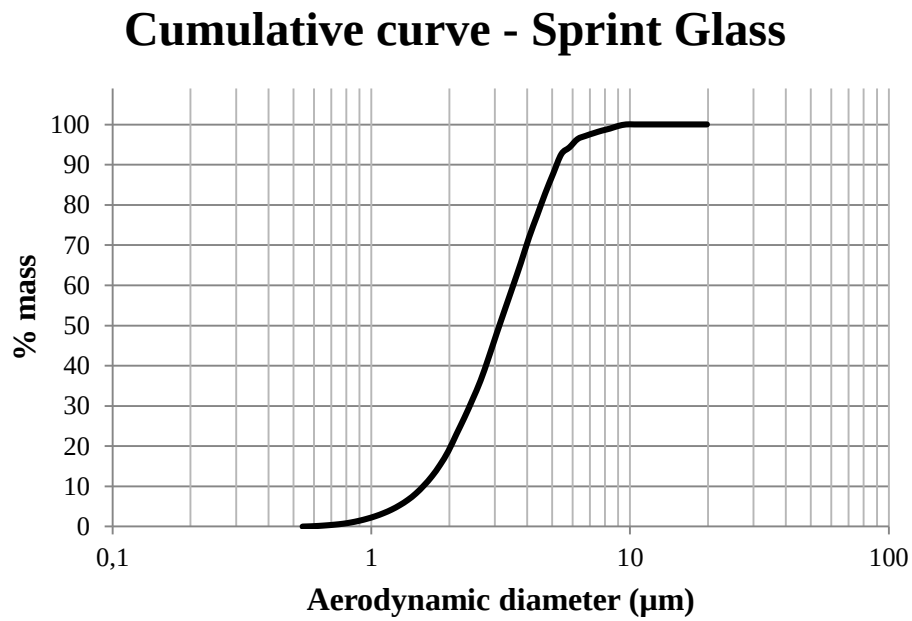

Figure 4.7 The cumulative curve for Johnson Diversey Sprint Glass Pur-Eco.

The MMD value was then read at 50 % of the total mass. The MMD values for all the products are presented in Table 4.3.

Figure 4.8 shows a typical example of the data print out from the Malvern Mastersizer were the MMD value (denoted D(v, 0.5)) can be found in the left column, this for Johnson Diversey Sprint Glass Pur-Eco.

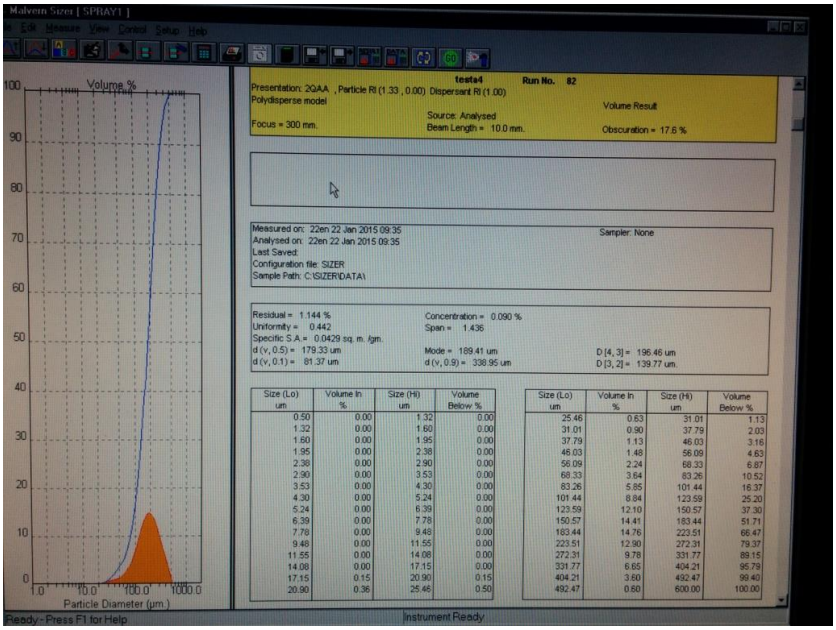

Figure 4.8 Data print out from the Malvern Mastersizer for Johnson Diversey Sprint Glass Pur-Eco. The orange curve is the size distribution and the blue curve is the cumulative curve.

However, for some of the products the data from the Malvern Mastersizer could look like the print out shown in Figure 4.9, this for Ajax Universal.

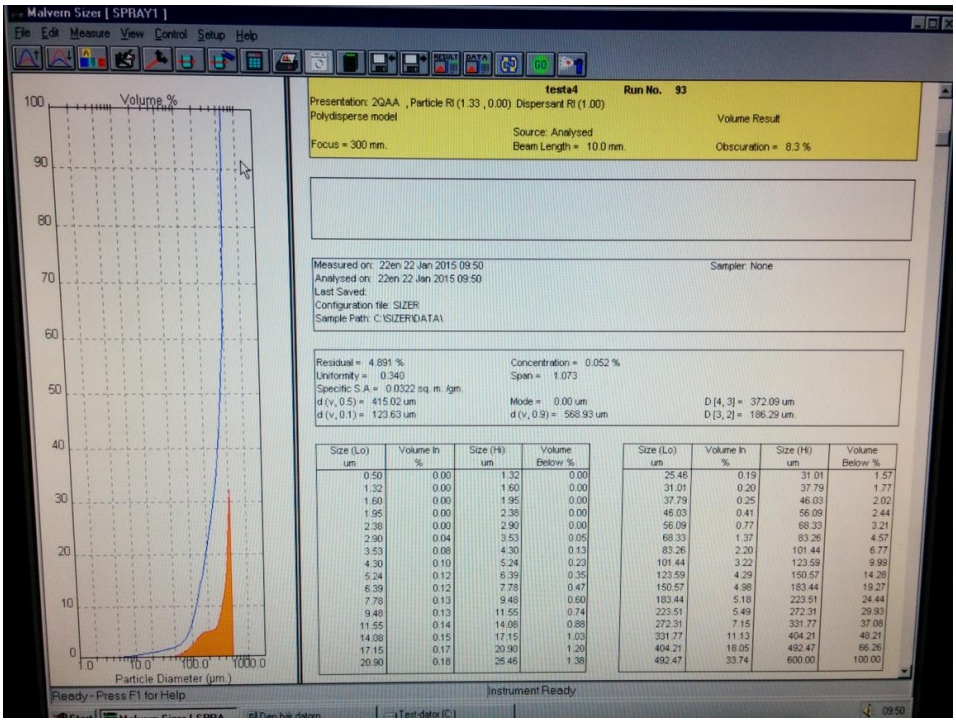

Figure 4.9 Data print out from the Malvern Mastersizer for Ajax Universal. The orange curve is the size distribution and the blue curve is the cumulative curve.

From this figure it is apparent that the actual size distribution cannot be determined since a normal distributed curve is not achieved and the MMD value seems to be above 600 µm.

Table 4.4 shows the MMD values derived from both the Malvern Mastersizer and the APS.

Table 4.4 The MMD values derived from the Malvern Mastersizer and the APS.

Product	**Mean MMD Malvern (µm)**	**Rel. SD MMD Malvern (%)**	**MMD APS (µm)**
Ajax Bathroom	125.8	9	4.2
Ajax Crystal Clean	249.1	15	3.2
Ajax Universal	415****	-----	3.8
Johnson Diversey TASKI Sani 100 free*	528****	-----	3.4
Johnson Diversey Sprint Glass Pur-Eco	179.6	4	3.1
Johnson Diversey Sprint Spitfire Spray	513****	-----	1.8

*Separate bottle was used on which the nozzle was turned 270 degrees to provide a spray stream similar to Ajax Bathroom (for comparability).
****One MMD value obtained from a poor size distribution (as shown in Figure 4.9).

To be able to validate the APS results the source strength ratio (the ratio of $\dot{m}(particles)$ and $\dot{m}(total)$) was compared to the particle diameter ratio as described in equation 3.5. Table 4.5 shows the value for these two ratios and their relation factor.

Table 4.5 The source strength ratio, the particle diameter ratio and the relation factor. The source strength ratio and the particle diameter ratio have been multiplied with 100 for comparison in percentage.

Product	**Source strength ratio (A) (%)**	**Particle diameter ratio (B) (%)**	**Relation factor (A/B)**
Ajax Bathroom	0.00018	0.00043	0.42
Ajax Crystal Clean	0.00030	0.00021	1.43
Ajax Universal	**	0.00008****	-----
Johnson Diversey TASKI Sani 100 free*	0.00204	0.00003****	68.00****
Johnson Diversey Sprint Glass Pur-Eco	0.00134	0.00052	2.58
Johnson Diversey Sprint Spitfire Spray	0.000015***	0.000004****	3.75****

*Separate bottle was used on which the nozzle was turned 270 degrees to provide a spray stream similar to Ajax Bathroom (for comparability).
**Too low concentrations were achieved and the source strength could not be simulated.
***This value was obtained from a poor fitting.
****One MMD value obtained from a poor size distribution (as shown in Figure 4.9).

A relation factor close to 1 means that there is a good correlation between the two measurement techniques (the APS and the Malvern Mastersizer) and that the data obtained from the APS is reliable and can be used for further analysis.

4.3 Pre-exposure dose-response study

One window cleaning spray was chosen for the human pre-exposure study.

For all the following box plots the bottom box line shows the 25 % quartile (the value below which 25 % of the data lies), the top box line shows the 75 % quartile and the line in the box show the median value. The error bars and outlier values, defined as 1.5 IQR (interquartile range) outside the box lines, are also included.

Figure 4.10 and 4.11 show the results of the tear film break-up time (BUT) measurements after exposure. Figure 4.10 shows the measured values in seconds while Figure 4.11 shows the percentage of the reference value.

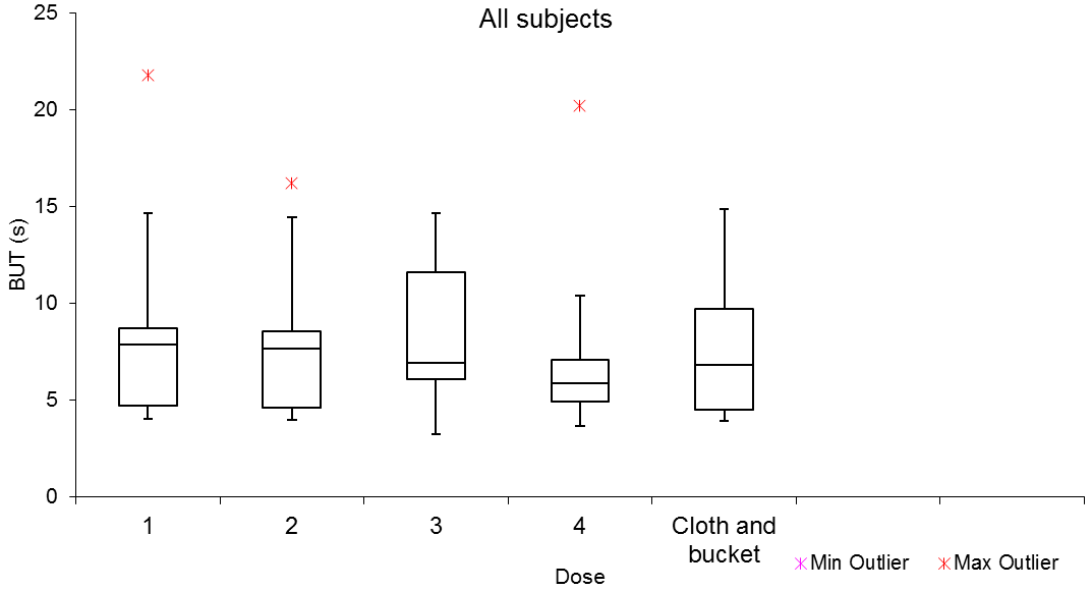

Figure 4.10 The BUT results after exposure in seconds.
The x-axis shows the different doses where 1 is the lowest spray dose and 4 is the highest spray dose.

Figure 4.10 shows a tendency for decreasing (median) tear film break up times with increasing spray dose, but with values consistently under 10 seconds (usually the value set for below which the eye is considered dry).

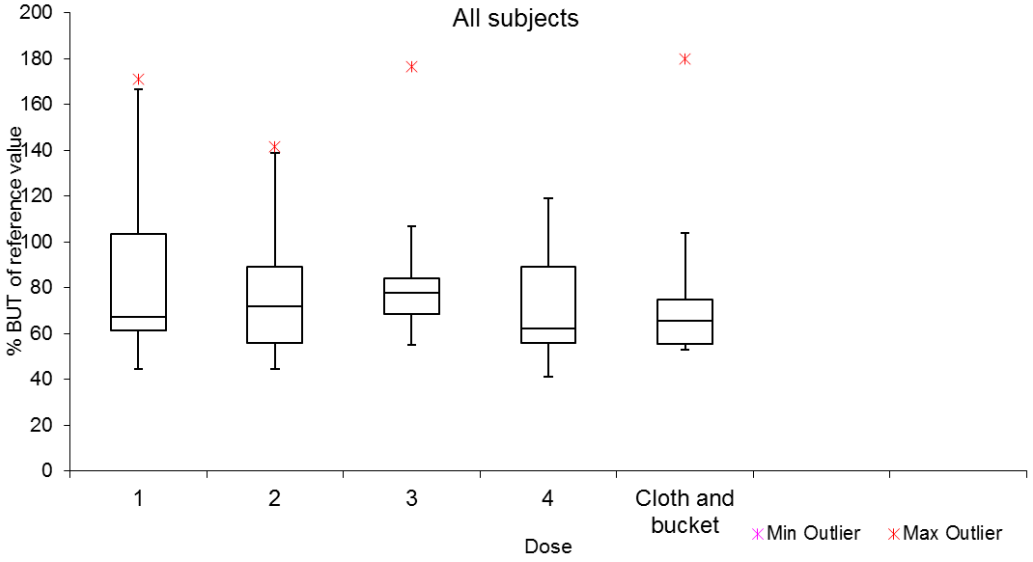

Figure 4.11 The BUT results after exposure in percentage of the reference value.
The x-axis shows the different doses where 1 is the lowest spray dose and 4 is the highest spray dose.

Figure 4.11 does not show the same correlation, but it can be noticed that all the median values are below 100 % of the reference values.

Figure 4.12 shows the results of the PNIF measurements after exposure as a percentage of the value before exposure.

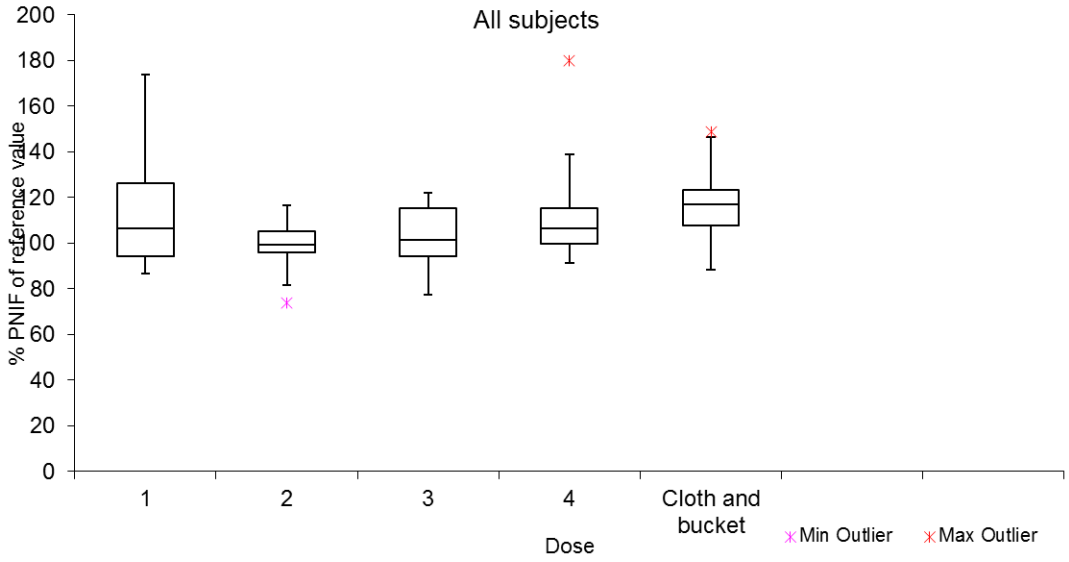

Figure 4.12 The PNIF results after exposure in percentage of the value before exposure. The x-axis shows the different doses where 1 is the lowest spray dose and 4 is the highest spray dose.

This figure shows that the median values are around or slightly higher than 100 % of the reference values.

Figure 4.13 shows the results of all the nose symptoms increase, from the questionnaire during exposure as a percentage of the value before exposure. Values that were lower "during exposure" than "before exposure" has been set to zero for the purpose of here just looking at any increase.

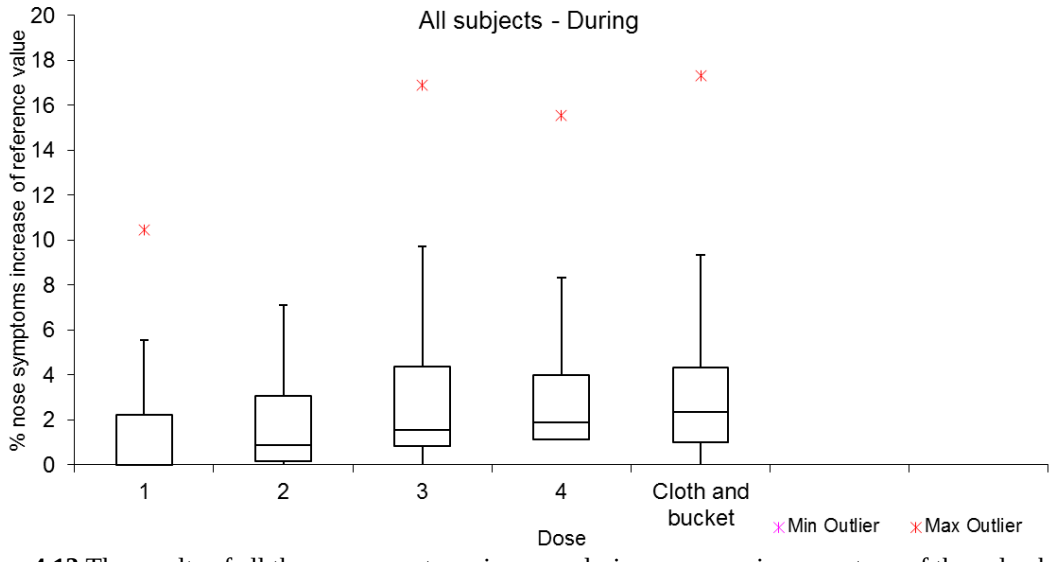

Figure 4.13 The results of all the nose symptoms increase during exposure in percentage of the value before exposure. The x-axis shows the different doses where 1 is the lowest spray dose and 4 is the highest spray dose.

This figure show a tendency of increasing nose symptoms with increasing spray dose.

Figure 4.14 shows the results of all the eye symptoms increase, from the questionnaire during exposure as a percentage of the value before exposure. Values that were lower "during exposure" than "before exposure" has been set to zero for the purpose of here just looking at any increase.

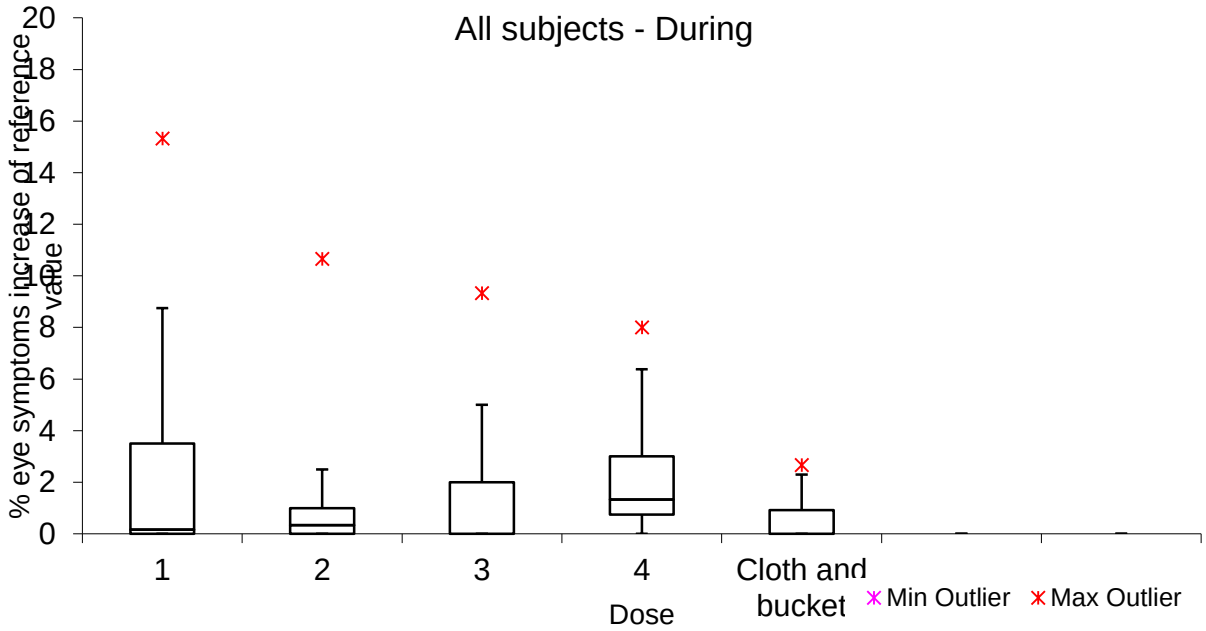

Figure 4.14 The results of all the eye symptoms increase during exposure in percentage of the value before exposure. The x-axis shows the different doses where 1 is the lowest spray dose and 4 is the highest spray dose.

This figure does not show the same correlation between increasing eye symptoms with increasing spray dose.

Correlations between different measurements or symptoms was investigated. Figure 4.15 shows the correlation between the BUT measurements and the PNIF measurements, both in percentage of the reference value (before exposure).

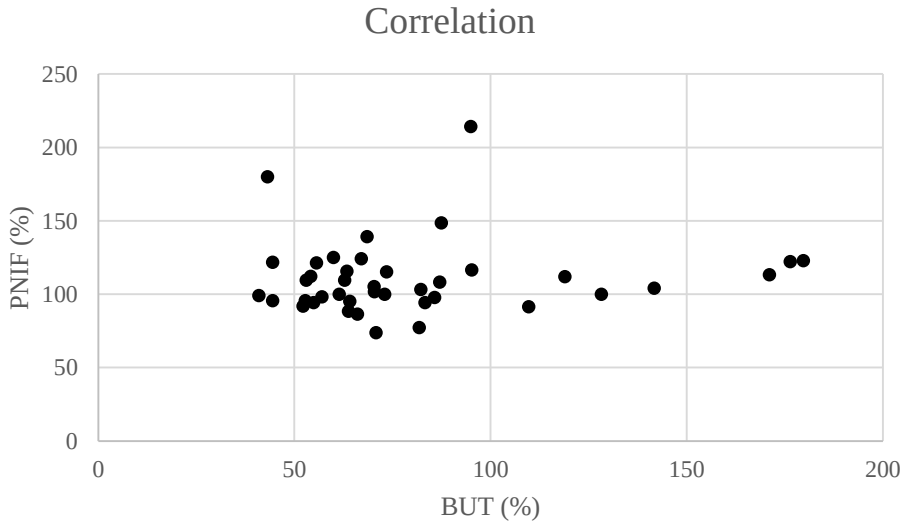

Figure 4.15 Correlation between BUT and PNIF in percentage of reference values.

However, no apparent correlation can be seen between these two measurements.

5. Discussion, conclusions and further research

5.1 Product identification and selection

Based on the phone survey, two general conclusions could be drawn. First of all, spray use is most common when cleaning bathrooms as well as windows and mirrors. Second, the most common products used by the responding companies were products from Johnson Diversey and Ajax. These conclusions were also consistent with the finding from the survey report (EPHECT, 2012) mentioned above.

5.2 Initial test measurements

During the measurements in the exposure chamber with the test spray products, the SMPS readings showed no significant change in particle concentration while the APS data did show particle concentration increase, however quite low. These results suggested that the particles from the spray products were larger than what the SMPS can measure, but in the size range of what the APS could register. The APS was hence chosen for the measurements of the selected products because of these findings.

Due to that an AER of only 0.5 h^{-1} was upheld through the exposure chamber, changes of the climate settings (temperature and RH) from the conditioning system adapted slowly. As a result of this low concentration and slow adaption of the climate settings in the exposure chamber, the experimental volume was chosen for the characterization of the products. The experimental volume also provided a smaller, easier-to-handle setup with faster climate setting changes and with the attached glove minimizing personal exposure.

5.3 Concentration uniformity

During some preliminary mass fraction measurements in the experimental volume, with the fan on, it was noticed that the variation between different measurements (with the same product) was quite large. One possible reason for this large variation was the fan, which both might affect the spray stream (blowing droplets in other directions than the spray direction), but also the papers on the wall (making them flicker, with the risk of not collecting all the droplets depositing on the wall) creating unreliable results. This was why measurements without the fan were preferable. As seen in the results from the concentration uniformity measurements without the fan (section 4.2.1.2) the uniformity was quite good in the whole volume with a variation of about 11 %. This variation was assessed as good enough and accepted, resulting in that the fan was removed for the characterization of the selected products.

5.4 Airborne mass fraction

A general conclusion that can be drawn from the results of the airborne mass fraction measurements (section 4.2.2) is that the window cleaning sprays generally has a high airborne mass fraction compared to the sprays for stains and all surfaces.

The bathroom product Johnson Diversey TASKI Sani 100 free did however have the highest airborne mass fraction, but also the highest standard deviation and relative standard deviation. This was the product tested with a separately purchased spray bottle and this bottle did not show the same quality as the bottles of the complete spray products. When used, this bottle was not always able to provide a steady spray stream, which could result in that a smaller volume was

sprayed out, or that the spray stream did not reach the wall, resulting in a high airborne mass fraction.

An observation made during the airborne mass fraction measurements was that the window cleaning products had a much wider spray area than the other sprays, which could have contributed to the high airborne mass fraction. One possible source of error during the airborne mass fraction measurements could be that the paper area was not large enough to collect all the droplets and what was not then weighed in the papers would be assumed to be in the air. Another source of error is that some large droplets could sediment to the ground almost directly after exiting the bottle (due to their large size) and thereby not be included in the paper weight, but at the same time not being suspended in the air. This last remark however is probably true for all the products, which would mean that the airborne mass fractions would be a bit lower, but the ratio between the different products would be the same.

The wide spray area for the window cleaning sprays is created due to the configuration of the spray nozzle. The two window cleaning sprays had flattened nozzles compared to the other products with more sharp nozzles. Due to this specific design, it would be interesting in the future to examine the characteristics of the products if the nozzles were switched.

Finally for the future, the experimental setup for airborne mass fraction measurements should be improved and optimized for better and easier-to-handle setup, foremost with regard to the paper-setup. Thicker, more absorbent papers should be considered, to ensure maximum collection of droplets on the wall, and an easier hanging setup (maybe with nails on the wall) to exclude the need for extra pieces of tape, should be developed.

5.5 Source strength

The most important conclusion from the results from the source strength measurements (section 4.2.3) is that there will be a very low mass percentage of particles suspended in the air shortly after spraying. More than 99.9 % of the initial spray droplet mass will quickly evaporate to a gaseous phase (the particle/gas ratio in Table 4.3).

In the result table (Table 4.2) it can be seen that there is no source strength value (for particles) for Ajax Universal. This is due to that when this product was measured, not high enough particle concentrations were reached to be able to simulate the requested source strength values. There were similar problems with the Johnson Diversey Sprint Spitfire Spray product and only a few source strength values could be simulated, resulting in a poor regression fitting and hence an unreliable value.

For the future, these source strength measurements should be repeated to achieve a stronger validation of the results and statistical significance for more reliable conclusions.

5.6 Validation of APS data

As can be seen in the result table for MMD values (Table 4.4) the MMD value of the dried particles measured with the APS is around the same for all products, approximately 3-4 µm. The Johnson Diversey Sprint Spitfire Spray product however show an exception, but as stated above, there were a few problems with the data analysis for this product and this value may not be reliable.

As a remark, it can be stated that the concentration values used to determine the MMD values from the APS data were not adjusted for tube losses, however this should not have a large impaction on the results presented since the particle penetration was between about 90-99 % (losses of 1-10 %).

For the three products that got data print outs from the Malvern Mastersizer looking like that in Figure 4.9, where the size distribution curve never reversed after reaching a maximum value (which a normal size distribution would), the MMD value seemed to be above 600 µm. For further research it would therefore be interesting to measure the initial particle diameter with a long bench Mastersizer, which can measure particles up to 2 mm.

For the actual validation of the APS measurements the relation factors presented in Table 4.5 can be a good tool. Looking at the three products with somewhat reliable values, their relation factors are quite good (close to 1). The conclusion can thereby be drawn that the APS measurements are valid, at least for the products with which a high enough concentration can be achieved to do proper data analysis.

5.7 Further research for product characterization

In addition to the suggestions that has been made above, concerning future experimental work, a few general suggestions can be made. One area that would be interesting to investigate is how different temperatures and especially different settings of RH would effect the airborne mass fractions and the source strengths, since this could effect the evaporation. This would also be valid to determine for evaluation of different work environments.

The next step for characterizing the products would be to examine the chemical compositions of the dried particles and to identify which gases that are formed during spraying with the different products. The available product data sheets did not provide sufficient information about this.

Some specific things to consider for future experiments are first of all to develop a more stable APS measuring setup. During the work with this thesis the setup used for the APS measurements had to be reassembled every time the glass door was opened, since the measuring tube was mounted through the sealable opening in the glass door. This resetting may compromise the comparability between the different products, since the different products might not have been measured in the same way (even though I strived for as similar setups as possible).

Second, the characterization of the experimental volume should be repeated without the fan present in the volume. This to make sure no extra deposition losses were registered due to the extra surfaces (from the fan setup) present during the characterization.

Third, the surface being sprayed should be considered. The mass fraction measurements were performed by spraying against paper, but would there be a higher concentration in the air (due to droplets bouncing off the surface), leading to higher exposure, if the surface being sprayed was stainless steel or glass?

5.8 Pre-exposure dose-response study

A window cleaning product was chosen to make the exposure as realistic as possible since the exposure chamber contains a glass window. The window cleaning products also had higher airborne mass fractions, making the possible exposure greater and, for health purposes, more interesting to investigate than for example a spray for stains.

No statistical conclusions can be made with only eight subjects, who also showed large individual variations, but some trends can be seen.

Figure 4.10 shows a small trend of decreasing BUT values with increasing spray dose, suggesting that the tear film is destabilizing with increased exposure. However, many of the subjects had low BUT values from the beginning (low reference values) and BUT values under 10 seconds usually means that the eye is dry. The low reference values may be due to low RH in the surrounding room, outside the exposure chamber (where the BUT measures were done) or that the PNIF measurement affected the tear duct. These low reference values are one reason to why this trend is not seen in Figure 4.11, which shows the percentage of the reference value. One thing which can be seen in Figure 4.11, however, is that most of the BUT values after exposure are under 100 % of the reference value, suggesting that the tear film stability is affected by exposure to the cleaning spray.

Figure 4.12 shows the result from the PNIF measurements. Here the results suggest that the PNIF values are quite unaffected, in some cases even improving with increased spray dose (median values of about 100 % of reference or slightly higher). This could indicate that nasal obscuration actually could be reduced with increasing spray dose. However, the PNIF-measurements varied a lot giving unreliable results.

Figure 4.13 shows the result from the sum of the nose symptoms on the questionnaires. A small trend of increasing nose symptoms with increasing spray dose during cleaning spray exposure is seen. Figure 4.14 does however not show the same trend for the sum of the eye symptoms.

Finally, from the correlation plot shown in Figure 4.15 no clear conclusions can be drawn.

One tendency that can be seen in the BUT, PNIF and nose symptoms results is that the “cloth and bucket” dose actually gave results and symptoms comparable to those of the higher spray doses. One explanation for this could be that the bucket filled with the cleaning product is located beside the subject during the whole exposure, making it possible for the liquid to evaporate and causing a longer exposure than for the spray doses, where the liquid is inside a closed container when it is not used. As a short comment, it has been reported that some cleaning workers spray directly into the cloth when cleaning, thereby not being exposed to the spray aerosols or the aerosols evaporating from an open bucket.

To sum up, a small trend in decreasing BUT values and an increase in nose symptoms for increasing spray doses could be observed from the human pre-exposure study.

For future human exposure studies, the BUT measurements could be a valuable tool to estimate the effect on the eyes since the symptoms the subjects feel are not as apparent as those measured. However, subjects using contact lenses could, due to this, have less sensitive eyes and should maybe be excluded from future studies (or at least analyzed separately). Whether or not the PNIF examination effects the BUT measurements, should be further investigated and the PNIF measurement should perhaps be exchanged for another nose examination, such as

acoustic rhinometry, since it gave very inconsistent measures. The throat symptoms are not presented in this report, but were not that apparent. However, some protocol to measure the effect on the throat should be considered for future studies to really evaluate the effects on the full upper airways.

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Appendix A – Manuscript and questionnaire for phone survey

Hej! Jag heter Karin Lovén och jag ringer från Lunds Tekniska Högskola (avdelningen för Ergonomi och aerosolteknologi).

Jag deltar i ett forskningsprojekt där vi ska undersöka hur städpersonalens hälsa påverkas av valet av rengöringsprodukter. Det här är ett projekt som är finansierat av AFA försäkring.

Jag undrar nu om jag kan få ställa några frågor om ert företag och om vilka produkter ni använder.

Jag har sett på er hemsida att ni bla städar i/på butiker/kontor/skolor/sjukhus/hotell, stämmer det?

Använder ni rengöringsmedel som appliceras med sprayflaskor?

Om jag nu listar ett antal olika ytor kan du då tala om för mig om ni använder någon sprayprodukt när ni rengör dessa ytor? Om JA, vilken produkt?

Badrum (handfat, kakel mm)
Toaletter
Speglar
Fönster
Bordsytor (för arbete mm)
Lunchrums bord
Whitebordtavlor
Krittavlor
Rostfria köksytor
Spisplattor
Golvytor
Andra ytor

Varifrån köper ni in era rengöringsmedel?

Hur ofta ser ni över utbudet av produkter? Byter ni ofta produkter?

Stämmer det att ni bedriver er verksamhet i…?

Appendix B – General health questionnaire

Name: _____

Personal number: _____

Date: _____ Time: _____

Not at all **A lot**

Do you have a cold? 0——————————————————

Do you smoke? ☐YES ☐NO ☐Sometimes

If YES or Sometimes, when did you last smoke?_____

Do you have any eye disease? ☐YES ☐NO

If YES, which? _____

Do you use any type of eye medicine? ☐YES ☐NO

If YES, which? _____

Do you use contact lenses? ☐YES ☐NO

Do you use glasses? ☐YES ☐NO

Have you during child and adolescent years had allergic symptoms such as hay fever, asthma, atopic dermatitis or nettle-rash? ☐YES ☐NO

If YES, which? _____

Have you during the last year had any allergic symptoms?

☐YES ☐NO

If YES, which? _____

Are you generally sensitive to smells? ☐YES ☐NO

Do you have any chronic illness? ☐YES ☐NO

If YES, which? _____

Do you regularly take any medication? ☐YES ☐NO

If YES, which? _____

Do you experience any problems with the indoor air at home or at your work?

☐YES ☐NO

If YES, which? _____

Do you practice advanced meditation? ☐YES ☐NO

BUT reference

Right eye	**Left eye**
_____s	_____s
_____s	_____s
_____s	_____s

General health after the whole exposure day

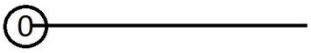
Appendix C – Before exposure questionnaire

Name: _____

Time: _____

Symptoms right now:

Mark on the line your symptoms, like this 

If you don't experience any symptoms at all, circle the zero, like this 

	No symptoms	**A lot of symptoms**
1. Itchy nose	0	
2. Runny nose	0	
3. Stinging feeling in the nose	0	
4. Tingling feeling in the nose	0	
5. Dryness in the nose	0	
6. Nasal congestion	0	

7. If you have symptoms in the nose, where do you feel these symptoms (close to the nostrils, back to the throat, or in some other way)?_____

_____

8. How many times have you sneezed during the last 10 minutes?_____

	No symptoms	**A lot of sympoms**
9. Itchy eyes	0	
10. Runny eyes	0	
11. Stinging feeling in the eyes	0	
12. Dry eyes	0	
13. Cough	0	
14. Dryness in the throat	0	
15. Whistle, breathlessness and/or chest tightness	0	

PNIF before exposure

_____ l/min

_____ l/min

_____ l/min

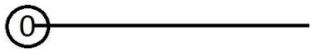
Appendix D – During exposure questionnaire

Name: _____

Time: _____

Symptoms *<u>when it was most apparent</u>*:

Mark on the line your symptoms, like this 

If you don't experience any symptoms at all, circle the zero, like this 

	No symptoms	**A lot of symptoms**
1. Itchy nose	0	
2. Runny nose	0	
3. Stinging feeling in the nose	0	
4. Tingling feeling in the nose	0	
5. Dryness in the nose	0	
6. Nasal congestion	0	

7. If you have symptoms in the nose, where do you feel these symptoms (close to the nostrils, back towards the throat, or in some other way)?_____

_____

8. How many times have you sneezed during the last 10 minutes?_____

	No symptoms	**A lot of symptoms**
9. Itchy eyes	0	
10. Runny eyes	0	
11. Stinging feeling in the eyes	0	
12. Dry eyes	0	
13. Cough	0	
14. Dryness in the throat	0	
15. Whistle, breathlessness and/or chest tightness	0	
16. When it was most apparent, how strong smell did you experience?	0	
17. When it was most apparent, how ***bothered*** were you by unpleasant smell?	0	

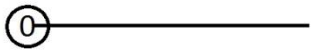
Appendix E – After exposure questionnaire

Name: _____

Time: _____

Symptoms right now:

Mark on the line your symptoms, like this 

If you don't experience any symptoms at all, circle the zero, like this 

	No symptoms	**A lot of symptoms**
1. Itchy nose	0	
2. Runny nose	0	
3. Stinging feeling in the nose	0	
4. Tingling feeling in the nose	0	
5. Dryness in the nose	0	
6. Nasal congestion	0	

7. If you have symptoms in the nose, where do you feel these symptoms (close to the nostrils, back to the throat, or in some other way)?_____

_____

8. How many times have you sneezed during the last 10 minutes?_____

	No symptoms	**A lot of sympoms**
9. Itchy eyes	0	
10. Runny eyes	0	
11. Stinging feeling in the eyes	0	
12. Dry eyes	0	
13. Cough	0	
14. Dryness in the throat	0	
15. Whistle, breathlessness and/or chest tightness	0	

PNIF after exposure

_____ l/min

_____ l/min

_____ l/min