Stellingen behorende bij het proefschrift
Development of a laser mass spectrometer for aerosols
door Olaf Kievit

Aangezien een deeltjesbundel gevormd wordt onder invloed van traagheid is het onmogelijk om selectiviteit met betrekking tot deeltjesgrootte volledig te onderdrukken.

De karakteristieke afmetingen van een zgn. Mach-conus worden volledig beschreven door de vergelijking \( \frac{L_c}{D} = c_1 \left( \frac{p_0}{p_b} \right)^{\frac{3}{2}} \).

Wanneer de laserintensiteit gevarieerd wordt kan men drie ionisatie-regimes onderscheiden. Bij lage intensiteit worden de moleculen vrijwel intact van het deeltje vrijgemaakt, zodat er relatief grote ionen ontstaan. Bij een hogere intensiteit zal door plasmavorming de fragmentatie toenemen, zodat er kleinere ionen ontstaan. Bij extreem hoge intensiteit ontstaan er weer grotere ionen en clusters. Het is onduidelijk of deze als zodanig worden losgemaakt, of dat zij door agglomeratie ontstaan.

Het ontbreken van signalen afkomstig van ammoniumsulfaat bij de analyse van deeltjes die tevens natrium- en kaliumchloride bevatten duidt op een inhomogene verdeling van de samenstellende componenten.

Een experiment mislukt nooit; het levert hooguit resultaten op die vooraf niet verwacht werden.

Een verzameling deeltjes kan alleen dan monodispers worden genoemd wanneer zij uit één deeltje bestaat. Het is zowiezo nutteloos een meetresultaat te rapporteren zonder ook de nauwkeurigheid te geven.

Een goede maat voor de welvaart van een land moet behalve de economische situatie ook zaken als het milieu en het welzijn van de inwoners omvatten. Het Bruto Nationaal Product voldoet duidelijk niet aan dit criterium.

Door de recente overstromingen van de grote rivieren heeft het imago van Nederland als dijkenbouwende natie meer immateriële schade opgelopen dan dat er aan concrete materiële schade is geleden in de overstroomde gebieden.

De vernieuwingsdrang die met name producenten van wasmiddelen en software tentoonspreiden is niet gericht op verbetering van het produkt, maar op voortzetting van het bedrijf.

De vaak geroemde Nederlandse tolerantie is niets anders dan vergaande onverschilligheid.

De gewoonte van veel jonge kinderen om erg vroeg wakker te worden is het gevolg van overbezorgdheid van de ouders. Omdat deze ten onrechte denken dat een x aantal uren slaap noodzakelijk is worden de kinderen vaak te vroeg naar bed gebracht.
Development of a laser mass spectrometer for aerosols

De ontwikkeling van een laser-massaspectrometer voor de analyse van aërosolen

Olaf Kievit
Development of a laser mass spectrometer for aerosols

De ontwikkeling van een laser-massaspectrometer voor de analyse van aërosolen

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Delft, 
op gezag van de Rector Magnificus Prof.ir. K.F. Wakker, 
in het openbaar te verdedigen ten overstaan van een commissie, 
door het College van Dekanen aangewezen, 
op dinsdag 2 mei 1995 te 13.30 uur 
door

Olaf KIEVIT

scheikundig ingenieur,

geboren te Rotterdam.
CIP-DATA KONINKLIJKE BIBLIOTHEEK DEN HAAG

Kievit, Olaf

Development of a laser mass spectrometer for aerosols / Olaf Kievit. - [S.l. : s.n.]. - III.
Thesis Technische Universiteit Delft. - With ref. - With summary in Dutch.
ISBN 90-9008121-6
Subject headings: aerosols ; mass spectrometry.

Copyright © 1995 by O. Kievit
All rights reserved.

No part of the material protected by this copyright notice may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system, without permission from the publisher.
Voor Bertina en Daphne.

She's got eyes of the bluest skies
As if they thought of rain
I hate to look into those eyes
And see an ounce of pain

(Guns N' Roses, Sweet child o' mine)
The work described in this thesis was supported by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for Scientific Research (NWO) and the Technology Foundation (STW).
Table of content

1 Introduction
  1.1 Scope of this thesis ........................................... 1
  1.2 Single particle sizing ........................................ 1
  1.3 Single particle chemical analysis: off-line techniques .... 2
  1.4 Single particle chemical analysis: on-line techniques ... 4
  References ......................................................... 7

2 The aerosol beam
  2.1 Introduction .................................................. 11
  2.2 What is an aerosol beam? ..................................... 11
  2.3 Characteristics of the ideal aerosol beam generator ..... 13
    2.3.1 Sample flow rate ..................................... 13
    2.3.2 Ultimate vacuum ....................................... 13
    2.3.3 Shock wave formation .................................. 13
    2.3.4 Transport efficiency and beam dimensions .......... 13
    2.3.5 Particle size effects .................................. 14
  2.4 Translation of the characteristics into design parameters
    2.4.1 Parameter dictated by the sample flow rate: pump
      speed ....................................................... 14
    2.4.2 Parameter dictated by the sample flow rate:
      nozzle diameter .......................................... 15
    2.4.3 Parameter dictated by the ultimate vacuum:
      number of pumping stages ................................ 17
    2.4.4 Parameters dictated by shock wave formation:
      location of the skimmers ................................ 18
    2.4.5 Parameter dictated by the beam dimensions: size
      of the second skimmer ................................... 20
    2.4.6 Parameter dictated by the transport efficiency and
      particle size effects: nozzle geometry .................. 21
  2.5 Practical performance of the aerosol beam generator ..., 28
    2.5.1 Experimental setup .................................... 28
    2.5.2 Sample flow rate ...................................... 30
    2.5.3 Ultimate vacuum ...................................... 31
    2.5.4 Aerosol beam dimensions ................................ 32
    2.5.5 Transport efficiency ................................... 34
  References ......................................................... 35

Appendix 2A Calculation of the skimmer diameter .......... 37
Appendix 2B Listing of the user-defined subroutine for
  calculating the drag coefficient ............................ 38
Appendix 2C Calculation of the axial flow field .......... 40
Appendix 2D Calibration curve for the fluorescence
  measurements .................................................. 43
3 Detection and sizing
3.1 Introduction .............................................. 45
3.2 Theory of light scattering ............................... 47
  3.2.1 The physics of light scattering ................. 47
  3.2.2 Light scattering by a sphere: Mie theory .... 47
  3.2.3 Limitations of Mie theory and alternative theories ............................................. 49
3.3 Light scattering experiments ......................... 52
  3.3.1 Choice of components ............................ 52
  3.3.2 The experimental setup .......................... 54
  3.3.3 Data collection and storage ...................... 56
  3.3.4 Experimental procedure .......................... 56
3.4 Model predictions and interpretation of the experimental results ............................................. 58
  3.4.1 Model description .................................. 58
  3.4.2 Modelling results ................................ 62
  3.4.3 Data reduction ................................... 65
  3.4.4 Experimental results: detection efficiency .... 67
  3.4.5 Experimental results: area ratio ............... 68
  3.4.6 Experimental results: peak width ............... 70
3.5 Conclusions and discussion ......................... 73
References .................................................. 74
Appendix 3A Calculation of beam and focus diameters using the ABCD law ............................................. 77
Appendix 3B Calibration curves for the photomultipliers 5083 and 5084 ............................................. 80
Appendix 3C Kernel estimators of the experimental light scattering data for 0.501 μm PSL and 4 μm corn oil particles ............................................. 82

4 Laser-ionization of aerosol particles
4.1 Introduction .............................................. 91
4.2 The interaction of radiation with an aerosol particle ............................................. 91
  4.2.1 General description of the interaction physics ............................................. 91
  4.2.2 Moderate irradiance: the DVR-model ............ 93
  4.2.3 High irradiance: ionization and plasma effects ............................................. 97
4.3 Experimental section ..................................... 102
  4.3.1 The vaporization/ionization laser ............... 102
  4.3.2 Triggering of the HY1200 ......................... 103
  4.3.3 Ion formation; experimental and model results ............................................. 105
References .................................................. 108
Appendix 4A Absorption centres and morphology dependent resonance ............................................. 110
5 Time-of-flight mass spectrometry
  5.1 Introduction ............................................. 113
  5.2 Theory of operation ...................................... 113
  5.3 Experimental setup ..................................... 116
  5.4 Experimental results .................................... 118
      5.4.1 General discussion .................................. 118
      5.4.2 Degree of ionisation ................................ 121
      5.4.3 Reproducibility ..................................... 123
  5.5 Conclusions ............................................. 127
References .................................................. 128
Appendix 5A Selection of mass spectra. .................... 129

Summary and conclusions .................................. 139

Samenvatting ................................................. 141

Dankwoord, Danksagung, Acknowledgements ............... 143

Curriculum vitae ........................................... 145
Introduction

1.1 Scope of this thesis

Although it is not realized by many people, there are airborne particles all around us. If we want to measure the size of individual particles suspended in the air, there are several off-the-shelf techniques to choose from. However, no standard measuring technique is available if on-line information on the chemical composition of individual particles is the ultimate object. Yet there are plenty of situations where it is desirable to know both the size and chemical composition of single particles (Friedlander 1977). The combined knowledge of size and composition can be considered the fingerprint of a particle, which can be of use in a number of applications. In environmental science and industrial hygiene it can help to determine the origin of particles found in the atmosphere and likewise it can help to locate emission sources in clean room technology. Furthermore size and composition are key parameters in the behaviour of aerosol reactors, and these should therefore be known to enable on-line control of aerosol processes.

This thesis describes the development of an instrument capable of on-line determination of size and chemical composition of single aerosol particles. It employs aerosol beam techniques to sample the particles from the aerosol, and section 2 is devoted to this part of the instrument. In the aerosol beam the particles are detected and sized using light scattering, which is the subject of section 3. After a particle has been detected it is hit by a powerful laser pulse and laser-particle interactions are treated in section 4. The ions generated by the laser-induced fragmentation process are analyzed by time-of-flight mass spectrometry, which is described in section 5. Finally, the instrument performance and other results are discussed in the ‘summary and conclusions’. The remainder of this introduction will give an overview of the techniques currently available for measuring the size and composition of single aerosol particles. It will serve to place the present work in a broader context.

1.2 Single particle sizing

Particle diameters can be determined in an on-line mode of operation through a number of techniques, which can roughly be divided into three categories: optical techniques, electrical techniques and combined physical techniques (see e.g. Willeke and Baron 1993). In optical instruments the interaction of aerosol particles with the incident light serves as a basis for
the real-time measurement of particle size. Important features of optical measurement methods include high sensitivity, fast response, and the possibility of in-situ analysis. A disadvantage of these methods is that the measured quantities, light extinction and scattering, not only depend on the size of the particles but also on their optical properties. Consequently, substantial errors can be introduced if the particles under investigation are very different from the particles used for calibration of the instrument. The electrical properties of aerosol particles are also widely used for measuring the size of particles in the airborne state. Charged particles placed in an electric field move with a velocity which is a function of particle size and charge. If the particles have a known charge the size dependence can be utilized for particle sizing, as is done in the electrical mobility analyzer. Of the combined physical techniques the time-of-flight aerodynamic particle spectrometry is most widely applied. The operation of a time-of-flight aerodynamic particle sizer (not to be confused with a time-of-flight mass spectrometer) is based on the detection of scattered light pulses from single particles. The major difference between this instrument and conventional optical particle counters is the measured parameter. Instead of the scattered light intensity the instrument measures the velocity of a particle which is related to its aerodynamic diameter. Another well-known combined technique is applied in the differential-mobility analyzer. This instrument separates charged particles on the basis of their electric mobility after which they are counted by a condensation nucleus counter. A diffusion battery works in a similar way but in this case separation is achieved by diffusion. Modern commercial particle sizers allow the on-line measurement of particle size down to a few nanometres.

1.3 Single particle chemical analysis: off-line techniques

Standard single particle analysis techniques operate in an off-line mode. This implies that some kind of sampling device samples the particles onto a substrate before they can be analyzed. The most common techniques are X-ray probes, mass spectrometry and vibrational spectroscopy. The X-ray probes include electron probe X-ray micro analysis (EPXMA, see e.g. Reed 1975), scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDS, see e.g. Goldstein and Yakowitz 1987), particle-induced X-ray emission (PIXE, see e.g. Johansson and Campbell 1988) and X-ray photoelectron spectroscopy (XPS, see e.g. Briggs and Seah 1983). EPXMA and SEM/EDS are essentially identical methods capable of analysing particles down to diameters of approximately 50 nm, but for these small particles only major constituents are detectable. For large particles (\(d_p > 1 \mu m\)) the detection limit is in the order of 1000 ppm. With PIXE the detection limit is much lower (down to 10 ppm) and combined with the analysis of back-scattered particles (Rutherford Back Scattering, RBS, see Finstad and Chu 1988) additional information on light elements is available. At present these techniques are limited to particles larger than 1 \(\mu m\). Advantages of EPXMA and PIXE are that the bulk elemental
composition is obtained while the particle remains intact. XPS is a semi-quantitative surface analysis technique, which probes the first few atomic layers of the particle only. Janssen and Goldmann (1993) have successfully applied XPS to the real-time analysis of aerosol particles, but the instrumentation is still in the experimental stadium. Recently, the use of electron energy loss spectroscopy (EELS) as a microanalytical technique was demonstrated (Khoffer et al. 1989). This technique is still under development, but identification and quantification of the elementary composition seem possible for very thin samples. Finally, the Yokogawa Electric Corporation has developed a new commercial particle analyzer PT1000, which uses a microwave-induced helium plasma (He-MIP) to produce excited atoms from previously collected particles. The manufacturer claims to be able to detect Fe, Cu, Ca and Na (Takahara et al. 1993), but at present no independent results have been reported.

In contrast with these mentioned techniques molecular information can be obtained from Raman spectroscopy, infrared back scattering, and fourier transform infrared (FT-IR) spectroscopy. Commercial equipment for the Raman analysis of single particles has been available since 1979 (Dhamelincourt et al.) and the limitations of the technique are discussed by Ett and Blaha (1980). Infrared back scattering has been successfully applied to discriminate between sulphuric acid and ammonium sulphate aerosols (Mudd et al. 1982), but other applications have not yet been reported. FT-IR spectroscopy is a technique which is still being developed and Kellner and Malissa (1989) obtained good results with the analysis of aerosol particles collected on impactor stages. Unfortunately all of the listed spectroscopic techniques suffer from low sensitivity and they are, therefore, only suitable for studying major components. Laser-induced aerosol fluorescence (LIAF), developed by Niessner and coworkers (1991), is especially suitable for the detection of adsorbed polycyclic aromatic hydrocarbons (PAHs). With this technique, which is not intended for overall chemical analysis, detection limits down to 10 ng PAH/m³ have been achieved. Another promising technique is laser-induced breakdown spectroscopy (LIBS), which yields qualitative and quantitative data on a range of metals present in aerosols (Biswaas et al. 1987). At present applications are limited because detection limits are high, in the range of 200 μg metal/m³.

SIMS and LAMMS, two types of mass spectrometry, can successfully be applied to the off-line analysis of single particles, yielding both elemental and molecular information. Secondary ion mass spectrometry (SIMS) is a versatile analysis method capable of detecting all elements and, to a lesser content, compounds too (Newbury 1980). It is suitable for determining depth profiles in particles, down to the submicrometre range, with a lateral resolution of about 1 to 2 nm. Laser microprobe mass spectrometry (LAMMS, see e.g. Van Vaeck and Gijbels 1989, Kaufmann 1986) can be considered the off-line version of the analysis method described in this thesis. Commercial instruments like the LAMMA-500 (Leybold Heraus, Köln) and LIMA-2A (Cambridge Mass Spectrometry, nowadays Kratos, Manchester) have been available for over 15 years, although the
production has recently been stopped. Particles are collected on a suitable substrate, usually a filter or impactor stage, and vaporized and ionized by a short, high-intensity laser pulse. The particles are selected by the operator with the aid of a low power alignment laser. This treatment is one of the major limitations of the instrument. As a consequence it is not possible to analyze particles smaller than a few tenths of a micrometre. An upper limit of 1 to 2 micrometers exists because of the limited rate at which energy can be deposited into the sample. This rate depends on the focus diameter, laser power density and particle properties, as was found by Wieser and coworkers (1981). The ions produced by the vaporization/ionization process are usually analyzed by a time-of-flight mass spectrometer equipped with a reflectron. By varying the laser energy both surface and bulk concentrations can be obtained. Other advantages include the possibility of analyzing organic species and the speciation of salts containing nitrogen and sulphur. Furthermore the detection limits for trace analysis are rather low: usually in the ppm range. In general LAMMS analyses yield spectra with a shot-to-shot standard deviation of typically 20 to 50%. The results are therefore qualitative or semi-quantitative at best.

Each of the techniques described in this section requires the particles to be collected on a substrate and transferred to the instrument for analysis. This process is likely to cause changes in the sample. Particles collected on filters or impactors may form agglomerates or fragments as they collide with surfaces or other particles. Furthermore, chemical reactions between neighbouring particles can take place and volatile components may be lost. In conclusion it can be stated that a single particle analysis method can only be considered truly reliable if it is operated in an on-line mode. The next section will therefore be devoted to on-line techniques.

1.4 Single particle chemical analysis: on-line techniques

At present, there are only two methods described in the literature which are capable of single particle analysis in an on-line mode: atomic emission spectroscopy and mass spectrometry. With atomic emission spectroscopy, the particles are vaporized and ionized by either a laser spark (Radziemski et al. 1983) or an inductively coupled plasma (Bochert and Dannecker 1989). Information on the elementary composition of a particle is obtained by spectral analysis of the radiation emitted by the excited atoms and ions. The detection limits are element dependent and range from 100 to a few 1000 ppm.

In comparison with the atomic emission technique there have been far more studies on the subject of on-line analysis by mass spectrometry. Davis (1973) was the first one to report the analysis of airborne particles by the direct admittance of a stream of ambient air into the ion source of a mass spectrometer. Significant contributions were also made by Myers
and Fite (1975), Allen and Gould (1981), and Sinha, Friedlander and coworkers (Sinha et al. 1982, 1984; Giggy et al. 1989). In the early versions of the instrument the particles impinged directly upon a heated metal filament where the aerosol material was ionized by surface ionization. The ionization efficiency was highly dependent on the analyte ionization potential and only materials with low potentials (<8 eV) could be detected. Electron ionization is an alternative method, but in general the ionization efficiencies are low and the background is usually high due to residual gasses. Both thermal and electron ionization are generally combined with quadrupole or focal plane mass spectrometers. The relatively short time scale of the ionization process makes it impossible to obtain a complete mass spectrum. Much better results have been obtained with laser-induced fragmentation, as was first suggested by Dahneke (1980).

Sinha (1984) was the first to use laser-ionization for the real time analysis of microparticles. The particles in the aerosol beam are sized according to their velocity, measured by monitoring the scattered light pulses as they traverse through two helium-neon laser beams which have a known distance of separation. After a fixed time delay relative to the first scattered light pulse a particle is intercepted by a high power Nd:YAG laser pulse for its volatilization and ionization. The ions are monitored by a quadrupole mass spectrometer and results were reported for potassium biphthalate particles of 2 \( \mu \)m. Laser ionization offers a number of advantages:

- evaporation and ionization are highly efficient,
- it is generally applicable,
- both elemental and molecular information can be obtained, by control of the intensity,
- it is fast.

Some years later Marijnissen et al. (1988) published a paper proposing improvements on the technique (see Figure 1.1). These improvements include the usage of a single He-Ne laser beam to size and detect the particles and the application of a pulsed UV laser to enhance ionization.

![Figure 1.1 Outline of the apparatus proposed by Marijnissen et al. (1988).](image-url)
Furthermore the application of a time-of-flight mass spectrometer was suggested, which, unlike quadrupole or focal plane types, produces a complete mass spectrum from one single burst of ions.

Currently the development of an on-line chemical analysis technique for single aerosol particles is the subject of several research projects. McKeown et al. (1991) built an instrument in which particles from 3 to 10 μm can be detected through the collection of scattered light with an optical fibre. The detection signal triggers an excimer laser with a delay time of 2.1 μs. The delay causes size discrimination, because only particles with a certain velocity (range) are hit by the excimer laser pulse. A time-of-flight mass spectrometer yields the chemical composition of the particle. Although this setup has been applied successfully to several laboratory-generated aerosols, the mass resolution and signal-to-noise ratio are poor. Much better results were obtained by Hinz and coworkers (1994a), who used a pulsed nitrogen laser for particle vaporization and ionization, and light scattering from a single He-Ne laser for particle detection. With their system called LAMPAS (laser mass analysis of particles in the airborne state) they analyzed atmospheric particles with a mass resolving power of typically 450 to 600. The authors plan to determine the size of a particle from its velocity, measured either from the duration of the scattered-light pulse or from the trigger delay time if the particle is hit by the UV laser beam. A disadvantage of the physical separation of the detection and vaporization/ionization laser beams is that only particles with a specific velocity (i.e. a specific aerodynamic diameter) are analyzed. This effect can cause size biasing when particles are sampled from a polydisperse aerosol. Prather et al. (1994a) have developed a similar instrument, which they call aerosol time-of-flight mass spectrometer (ATOFMS). In this instrument particle velocities are measured by the same method as described by Sinha in 1984. An analog timing circuit measures the delay between the two scatter pulses and triggers the vaporization/ionization laser, which is either a pulsed CO₂ laser or a Nd:YAG laser. Although this configuration avoids the size dependency encountered by Hinz et al., it is very sensitive to alignment errors. Moreover particles can be missed by the vaporization/ionization laser when their trajectories are not exactly parallel with the aerosol beam axis. Prather and coworkers have minimized this problem by enlarging the vaporization and ionization volume, which consequently limits the maximum intensity that can be produced. Nevertheless good performance has been demonstrated for both organic and inorganic laboratory-generated aerosols, with a mass resolution of approximately 650.

A related technique, known as aerosol MALDI (matrix-assisted laser desorption ionization), has been developed by Murray and Russell (1994). It uses an aerosol beam as the interface between a liquid sample, for example from a high performance liquid chromatograph (HPLC), and a time-of-flight mass spectrometer. Efficient ionization is achieved by adding a suitable UV-absorbing matrix to the sample, and applications have been reported on the field of protein analysis. Unfortunately the technique suffers from a poor mass resolution, which can be as low as 6 at mass 700.
Recently several groups presented their results on the on-line chemical analysis of single aerosol particles at the International Aerosol Conference at Los Angeles California, held from August 29 to September 2 1994 (Ayre et al., Carson et al., Hinz et al., Kievit et al., Mansoori and Johnston, Murphy et al., Neubauer et al., Prather et al., Reents et al., Thomson et al., Weiss et al., and Yang et al. 1994). The fact that a complete conference session was devoted to the subject of aerosol mass spectrometry subscribes to the statement that there is currently great interest in this technique. It is to be expected that within a few years single particle laser-ionization mass spectrometry will have evolved into a useful analysis method.

References


On-line aerosol analysis by atomic emission spectroscopy, J. Aerosol Sci. 20, 1525-1528.

Practical surface analysis by Auger and X-ray photoelectron spectroscopy, John Wiley & Sons, Chichester.


Dahneke, B. (1980).
Sampling and analysis of suspended particles and vapors by continuum source particle beams. In Emission control from stationary power sources (A. Engel et al. eds.), AIChe Symp. Ser. 201/(76), AIChe, New York, pp. 134-143.

Surface ionization mass spectrometry of airborne particulates, Environ. Sci. Technol. 10, 278.


The aerosol beam

2.1 Introduction

The aerosol beam is an essential part of the instrument. It samples the particles from the aerosol and transports them to the measurement section. Ideally, the transport through the aerosol beam generator should be highly efficient and independent of the size of the particles. Furthermore the generator should have a high sample flow rate, and yet create a vacuum better than $10^{-4}$ Pa in the measurement chamber.

Unfortunately the ideal aerosol beam generator does not exist. The inertia of the particles will always result in transport losses, while the high pumping capacity necessary for the required pressure and flow rate brings high costs. This chapter will determine the characteristics of an aerosol beam generator which is optimized for application in this project. Using computational fluid dynamics (CFD), theoretical models, earlier results (Kievit 1990) and work from other authors, an optimal aerosol beam generator has been designed, given the practical constraints. Its performance will be discussed in relation to the requirements imposed by its application.

2.2 What is an aerosol beam?

When a gas is sucked through a small orifice into a low pressure chamber, it expands rapidly. The orifice, or nozzle, is typically a few tenths of a millimetre in diameter. The expansion of the gas causes the streamlines to diverge, as shown in Figure 2.1 (next page). Particles present in the gas cannot follow the streamlines, because of their inertia, and continue their rectilinear motion. This mechanism separates the particles from the gas and thus causes the actual formation of the aerosol beam.

Aerosol beams have been studied since 1964 (Murphy and Sears). Important contributions to this subject were made by Friedlander, Dahneke and coworkers (Israel and Friedlander 1967, Dahneke and Friedlander 1970, Dahneke et al. 1982, Estes et al. 1982). Recent applications of the aerosol beam include high-performance liquid chromatography (HPLC), where it is used as an interface between the gas chromatograph and a mass spectrometer (Willoughby and Browner 1984, Ligon and Dorn 1990). Commercial mass spectrometers with LC/MS-interfaces of this type are currently available.
Figure 2.1 Part of the flow pattern (i.e. contours of the stream function) calculated with the CFD-package Fluent®. The complete flow function is shown in Figure 2.5 (page 22).

The properties and applications of aerosol beams have been reviewed some years ago by Dahneke (1978). The diameter of the nozzle and the ratio of the pressures before and after the nozzle strongly influence the beam characteristics, including the gas flow rate and the dimensions of the beam. The solid angle of the cone formed by the particle trajectories is normally used to quantify the divergence of the beam. It can be reduced by sending the aerosol beam through a second limiting orifice, which is usually called a skimmer. In general, the divergence varies for particles of different sizes, as does the transmission efficiency.
2.3 Characteristics of the ideal aerosol beam generator

2.3.1 Sample flow rate

It is desirable to have a high sample flow rate. This shortens the time needed for analysis, which is especially advantageous when measuring low concentration aerosols. However, it should be noted that the cost and size of a vacuum pump increase rapidly with the pumping capacity. If the instrument is to be sold commercially it must not be too expensive and small enough to be used in field studies. These considerations impose restrictions upon the sample flow rate.

2.3.2 Ultimate vacuum

The function of the aerosol beam generator is to transport particles from the aerosol to the measurement section of the instrument. An important part of the measurement section is the time-of-flight mass spectrometer (tof-ms), which can only be operated properly at a pressure below $10^{-4}$ Pa. This means that the aerosol beam generator must be capable of reducing the ambient pressure of the aerosol under investigation ($10^5$ Pa) to the operating pressure of the order of $10^{-4}$ Pa.

2.3.3 Shock wave formation

If the pressure difference across the nozzle is big enough, the gas velocity exceeds the speed of sound and the expansion becomes supersonic. As in every supersonic expansion, shock waves can form in the aerosol beam generator, balancing the difference in pressure between the overexpanded supersonic jet and the background gas. Because of the shape of these waves, the phenomenon is usually referred to as a barrel shock or Mach cone. The waves disturb the gas flow and prevent the generator from working optimally. It is therefore necessary to design the aerosol beam generator in such a way that the formation of shock waves is minimized.

2.3.4 Transport efficiency and beam dimensions

Ideally, the instrument should analyze every particle which enters. This would limit the time needed to measure the large numbers of particles which are necessary to constitute a representative sample. Furthermore, it would facilitate the analysis of low-concentration aerosols, for example in clean room applications. The need for an efficient analysis implies that every step in the sampling process should be highly efficient. Specifically, the transport efficiency of the aerosol beam generator must be high, preferably 100%, which means that losses due to contact of particles with the walls of the generator must be minimized. In addition, every particle
transported to the measurement section must actually be available for
analysis, and must therefore pass through the measurement volume. The
dimensions of the measurement volume are limited by the focal size of the
sizing/detection laser, and the depth of focus. This sets limits to the
dimensions of the aerosol beam at the analysis location, restricting both
the diameter and the divergence of the beam.

2.3.5 Particle size effects

It is important that the efficiency of the sampling step is constant for the
entire sample, regardless of particle size. This is a condition which has to
be satisfied to ensure that the results of the analysis are representative.
Ideally, the transport efficiency of the aerosol beam generator itself would
also be independent of particle size. If this is not possible, the classifying
effect can either be used as a selection tool, or it can be compensated for
using calibration data. When sampling from a flowing gas, isokinetic
sampling is generally accepted as the best method for minimizing size
selectivity. Hangal and Willeke (1990) have recently presented a
comprehensive summary on this subject. With isokinetic sampling, the
dimensions of the sampling probe and the flow rate are chosen to yield a
suction velocity equal to the face velocity of the aerosol from which the
sample is drawn. Furthermore the probe has to sample isoaxially, which
implies that the direction of the sample flow has to be aligned with that
of the gas flow. In the instrument developed in this project the sample
flow rate is fixed (see also section 2.4.2), which leaves only the dimensions
of the sampling probe as a means for adjusting the suction velocity.
However, when the sample is to be drawn from a stagnant aerosol (calm
air conditions) the problem is more complicated, and size selectivity
cannot be avoided. In this case it is common practice to define the
conditions for representative sampling; the most frequently used criteria
are discussed by Vincent (1989).

2.4 Translation of the characteristics into design
parameters

2.4.1 Parameter dictated by the sample flow rate: pump speed

As was already pointed out in section 2.3.1, a high sample flow rate
shortens the time needed for a measurement. However, it implies a high
gas load on the first stage vacuum pump, although it doesn’t directly
influence the load on the second and third stage pumps. The reasons why
a three-stage system is chosen will be explained in section 2.4.4. A high
gas load on a vacuum pump means that a higher pump speed is required
to reduce the pressure to a given value. In general the pump speed of a
rotary pump is more or less constant over a pressure range from $10^3$ to $10^2$
Pa. The average value is usually specified in the technical data (Pneurop-
value). After studying the data on the double stage series from Edwards
it was found that the price increases rapidly when the pump speed exceeds 12 m³/hr, and that the weight rises dramatically when the pump speed exceeds 27.5 m³/hr. Taking speed, price and weight into account, it was decided that a rotary pump with a pump speed of 12 m³/hr is the best choice for our application.

With a given pump speed it is possible to estimate the sample flow rate. Because the gas flow from the first into the second stage is so small that it can be neglected, it can be assumed that all the gas sampled from the aerosol is removed in the first pumping stage. In vacuum technology it is customary to estimate the required pump speed from:

\[ Q = P \times S \]  
(2.1)

In this equation the gas load \( Q \) (expressed in mbar.m³/hr) is defined as the product of the pressure \( P \) and the volume flow rate \( S \). The equation holds both for the incoming flow rate (the sample flow rate) and for the outgoing flow rate (the effective pump speed). The effective pump speed will be somewhat lower than the value listed in the technical data due to the flow resistance of the components connecting the pump to the system. Assuming a pump speed of 12 m³/hr, this implies that the ratio of the sample flow rate over the reduced pressure can never exceed the value of \( 3 \times 10^{-8} \text{ m}^3\text{s}^{-1}\text{Pa}^{-1} \). If the aim is to reduce the pressure to \( 10^5 \text{ Pa} \), the sample flow rate will be in the order of \( 3 \times 10^{-5} \text{ m}^3/\text{s} \) (2 l/min).

### 2.4.2 Parameter dictated by the sample flow rate: nozzle diameter

If the ratio of the pressures before and after the nozzle exceeds a certain threshold value, the sample flow rate is completely determined by the diameter of the nozzle. This can be concluded from the Bernoulli equation for isentropic, frictionless flow of an ideal gas. Ashkenas and Sherman (1966) have found that friction, i.e. the effect of boundary layer formation, is negligible when the Reynolds number based on the nozzle diameter exceeds 300. In general this will be the case. In a one-dimensional system in the stationary state it can be shown that

\[ \frac{dp}{dv} = -\rho v \]  
(2.2)

where \( \rho \), \( v \) and \( p \) are the fluid density, the velocity and the pressure averaged across the flow. Since the pressure gradient \( dp \) is in the opposite direction of the velocity gradient \( dv \), the derivative \( dp/dv \) is always negative. Assuming continuity

\[ \rho v A = \text{constant} \]  
(2.3)

in which \( A \) is the local nozzle area, differentiation yields
\[ \frac{dp}{p} + \frac{dv}{v} + \frac{dA}{A} = 0 \]  \hspace{1cm} (2.4)

Combining Equations 2.2 and 2.4 gives

\[ \frac{dA}{dp} = A \left( \frac{1}{v^2} \cdot \frac{dp}{dp} \right) \]  \hspace{1cm} (2.5)

The propagation of a wave through a continuous medium is characterized by a single parameter \( c \) (the speed of sound), related to the compressibility

\[ \frac{dp}{dp} = \frac{1}{c^2} \]  \hspace{1cm} (2.6)

Hence,

\[ \frac{dA}{dp} = A \left( \frac{1}{\rho v^2} \cdot \frac{v^2}{c^2} \right) \]  \hspace{1cm} (2.7)

Usually, the magnitude of the local gas velocity is represented as the dimensionless Mach number \( M \), defined by \( M = \frac{v}{c} \). For an ideal gas the speed of sound is a simple function of the specific heat-ratio \( \gamma = c_p/c_v \), the universal gas constant \( R \), the local temperature \( T \) and the molar mass \( m \) of the gas molecules.

\[ c = \sqrt{\frac{\gamma RT}{m}} \]  \hspace{1cm} (2.8)

Realizing that the derivative \( dp/dv \) is always negative (Equation 2.2) it follows from Equation 2.7 that

\[ \frac{dA}{dv} < 0, \hspace{1cm} \text{when} \hspace{0.5cm} M < 1 \]  \hspace{1cm} (2.9)

Thus, for a converging nozzle the speed can never exceed the local speed of sound. At the nozzle exit plane, where the nozzle area has its minimal value \( A' \), the speed is equal to the speed of sound, and the Mach number \( M' = 1 \).

The local speed of sound can be calculated with the equations derived by Shapiro (1953) from elementary thermodynamics, which relate the local temperature, pressure and density of the gas to the stagnation properties,
denoted by the subscript 0. The stagnation condition of a gas describes the situation where there is no flow.

\[
\frac{T_0}{T} = 1 + \frac{\gamma - 1}{2} M^2
\]

(2.10)

\[
\frac{p_0}{p} = \left( 1 + \frac{\gamma - 1}{2} M^2 \right)^{\frac{\gamma}{\gamma - 1}}
\]

(2.11)

\[
\frac{\rho_0}{\rho} = \left( 1 + \frac{\gamma - 1}{2} M^2 \right)^{\frac{1}{\gamma - 1}}
\]

(2.12)

The critical ratios can be calculated by inserting \( M = M^* = 1 \). For air (\( \gamma = 1.40 \)) this yields:

\[
\frac{T^*}{T_0} = 0.8333 \quad \frac{p^*}{p_0} = 0.5283 \quad \frac{\rho^*}{\rho_0} = 0.6339
\]

The critical pressure ratio has to be exceeded if the magnitude of the gas velocity is to reach the speed of sound. Inserting \( T = T^* \) in Equation 2.8 yields the average magnitude of the axial velocity at the nozzle exit. The sample flow rate can be calculated by multiplying the velocity with the nozzle area, and correcting for the reduction in gas density. Assuming that the stagnation condition refers to \( T = 298 \text{ K} \) and \( p = 10^5 \text{ Pa} \), a sample flow rate of 2 l/min corresponds to a nozzle diameter of approximately 0.5 mm.

2.4.3 Parameter dictated by the ultimate vacuum: number of pumping stages

The aerosol beam generator must be capable of reducing the ambient pressure of the aerosol under investigation (\( 10^5 \text{ Pa} \)) to the operating pressure of the tof-ms (\( \leq 10^{-4} \text{ Pa} \)). As was shown in section 2.4.1, the first pumping stage is likely to reduce the pressure by a factor of 100 to 1000. Under the assumption that this factor is feasible for all pumping stages, it follows that at least three stages are needed to reach the required vacuum of \( 10^{-4} \text{ Pa} \). In reality it will be possible to reach a somewhat lower pressure with a three-stage system, because a higher pressure reduction factor is likely at the lower pressures.
2.4.4 Parameters dictated by shock wave formation: location of the skimmers

The divergence of the aerosol beam is limited by two orifices (skimmers) placed downstream from the nozzle. The location of these skimmers has to be chosen so as to prevent the occurrence of shock waves. Bier and Schmidt (1961) have examined this type of shock wave extensively, including the influence of the location of the skimmer. They found that the Mach disk will not be formed upstream from the nozzle when the distance between the nozzle and the skimmer is smaller than the distance $x_B$ at which the Mach cone has its maximum diameter $y_B$ (see Figure 2.2). Instead, the skimmer behaves as a second nozzle with its own Mach cone downstream. The major difference, however, is that the Mach number in the skimmer plane is greater than 1. The density of the supersonic flowing gas is low, and therefore the disturbing effects usually caused by a Mach disk are reduced significantly.

![Diagram of shock waves and skimmer location](image)

Figure 2.2 Characteristic lengths of the barrel shock.

Bier and Schmidt also found that for a fixed value of $\gamma$, the shape and size of the barrel shock are solely determined by the pressure ratio across the nozzle, $p_0/p_b$. Although not noted by the authors, their experiments show that all of the characteristic lengths ($L_c$) of the barrel shock, as defined in Figure 2.2, can be described by a single relation of the form

$$\frac{L_c}{D} = C_1 \left( \frac{p_0}{p_b} \right)^{C_2}$$  \hspace{1cm} (2.13)

which produces the size and location of the barrel shock within 5 %.
Table 2.1 lists the values of the two constants in Equation 2.14 for each of the characteristic dimensions specified in Figure 2.2, in the case of a diatomic gas ($\gamma = 7/5$). I have obtained these values by fitting the experimental data from Bier and Schmidt (1961), measured using Schlieren photographs, at pressure ratios ranging from 10 to 1000. Ashkenas and Sherman (1966) measured the location of the Mach disk ($x_M$) by impact pressure and free-molecule wire techniques. They modelled their results with Equation 2.13 and found slightly different values for the empirical constants $C_1$ and $C_2$. From their experiments, performed at pressure ratios between 15 and 17000, they calculated the constants to be 0.67 and 0.50 respectively. By assuming spherically symmetric inviscid flow, Dupeyrat (1981) found the same constants to have theoretical values of 0.65 and 0.50. Despite the very different methods through which those values were found they are all in reasonable agreement with Equation 2.13. The distance at which the diameter of the Mach cone is maximal ($x_B$) can be calculated with this equation. Assuming a downstream pressure of 100 Pa and a nozzle diameter of 0.5 mm, $x_B$ is found to be 7 mm. The distance between the nozzle exit and the first skimmer has to be smaller than this value, in order to shift the Mach disk location. In the present setup this distance is 4 mm. The reason for this is flexibility: a smaller nozzle diameter can be used when desired. With a distance of 4 mm, shock wave formation will be prevented for nozzle diameters down to approximately 0.3 mm.

Finally, it is also advisable to shift the Mach cone beyond the second skimmer. The distance at which the second skimmer has to be placed depends on both the pressure ratio and the diameter of the first skimmer. A diameter of 0.4 mm was chosen to guarantee an efficient particle transport and to yield a reasonable gas load on the second pumping stage, enabling the pressure at the third pumping stage to be reduced to approximately 0.1 Pa. According to Equation 2.13, a distance smaller than 5.5 mm should be used; the present setup uses 5 mm.

Table 2.1 Empirical constants for the characteristic lengths of a barrel shock, calculated from experimental data by Bier and Schmidt (1961).

<table>
<thead>
<tr>
<th>Characteristic length $L_c$</th>
<th>Empirical constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m)</td>
<td>$C_1$</td>
</tr>
<tr>
<td>$x_B$</td>
<td>0.47</td>
</tr>
<tr>
<td>$x_M$</td>
<td>0.74</td>
</tr>
<tr>
<td>$x_R$</td>
<td>0.89</td>
</tr>
<tr>
<td>$y_B$</td>
<td>0.38</td>
</tr>
<tr>
<td>$y_M$</td>
<td>0.31</td>
</tr>
<tr>
<td>$y_R$</td>
<td>0.45</td>
</tr>
</tbody>
</table>
2.4.5 Parameter dictated by the beam dimensions: size of the second skimmer

As will be shown in section 2.4.6, modelling studies with the CFD-package Fluent (copyright CREARE.X Inc.) indicate that the aerosol beam always has a significant divergence. Figure 2.3 shows how the beam diameter at a distance of 4 mm from the nozzle exit varies with particle size. These results have been calculated with a specific nozzle geometry, which will be described in detail later. Because the measurement volume is relatively small (roughly in the order of 0.1 mm) and located rather far from the nozzle exit (30 mm downstream), it is necessary to reduce the aerosol beam’s dimensions with the aid of the second skimmer. The location and diameter of this skimmer determine the ultimate divergence, which is only slightly dependent on particle size. However, excessive reduction of the beam’s dimensions is undesirable because it would make alignment very difficult. Furthermore experiments have shown that rapid clogging occurs when the orifice diameter becomes too small. Appendix 2A shows how the optimal value for the skimmer diameter can be calculated when the nozzle diameter, the location of the skimmer and the location and size of the measurement volume are chosen. For the given system the optimal diameter of the second skimmer is approximately 0.3 mm.

![Graph showing the relationship between particle size and beam diameter](image)

**Figure 2.3** Relation between particle size and diameter of the aerosol beam at a distance of 4 mm from the nozzle exit. Values were calculated for geometry B (see Figure 2.4), using Fluent.

20
2.4.6 Parameter dictated by the transport efficiency and particle size effects: nozzle geometry

The inertia of a particle plays an important role in the trajectory it follows. Inertia, and consequently also the size of the particle, will therefore influence the beam divergence, as defined in section 2.2. A computational fluid dynamics study with the software package Fluent® was undertaken to investigate the influence of particle size and nozzle geometry on the beam characteristics. It should be noted that Fluent® is not especially suitable for modelling low pressure gas dynamics or supersonic flow, and that the results are therefore to be used with caution. In the modelling study fixed pressure boundaries were imposed, and 10⁵ and 1 Pa were chosen as the inlet and outlet pressures. Compressibility of the fluid was taken into account by correcting the density for pressure variations. The temperature at the inlet was assumed to be 298 K. Turbulence effects were implemented using the $k\varepsilon$-model. The numerical grid was segmented and the spacing expanded, in order to create smaller cells in the area close to the nozzle exit. The distance between the wall and the first grid point was in the order of 10 μm, which ensures that the viscous sublayer - about 50 μm thick - can be modelled adequately. The results will show that nozzle A, depicted in Figure 2.4, has the highest transport efficiency if the particles are 2 μm or bigger; nozzle B is the better choice if particles smaller than 2 μm are to be analyzed.

![Diagram of nozzles A and B](image)

Figure 2.4 Geometrical outline of the nozzles A and B, modelled with Fluent®. The exit diameter is 0.5 mm in both cases.

Both nozzles A and B have been modelled to study the influence of nozzle geometry on beam divergence. Nozzle A can be manufactured by drawing a glass tube into a capillary, thus creating a smoothly converging flow channel. In principle, the nozzle diameter can be chosen freely. Nozzle B can be manufactured from metal, using standard machining techniques. The orifice is created by spark discharge machining, a technique which is capable of making holes down to 0.1 mm in diameter. With specially
designed spark electrodes it is possible to achieve diameters as small as 20 µm. The thickness of the nozzle wall should be of the same order of magnitude as the orifice diameter. Laser machining can be an alternative to the spark discharge technique, but it generally yields holes with a rim of solidified material around it. This could have a negative effect on the performance of the nozzle.

Figure 2.5 Contours of the flow function (calculated for nozzle B), showing that virtually all gas leaves the system via the top. The complete geometry, including first skimmer and vacuum pump, has been modelled.

Qualitatively, the flow field is similar for both nozzle geometries. The pressure shows a sharp drop at the nozzle exit, where the gas velocity increases rapidly and the stream lines are close to each other. The flow functions are similar as well, with small differences close to the nozzle exit. A contour plot, shown in Figure 2.5, indicates that only a very small fraction of the gas passes through the skimmer and that the rest is removed effectively by the vacuum pump.
The differences in the flow fields are manifested more clearly when the flow is seeded with particles. The standard Fluent program was extended with a user-defined subroutine to calculate the drag force at various flow conditions. The listing of this FORTRAN subroutine can be found in Appendix 2B. The stationary drag force can be written as

\[ F_D = \frac{\pi d_p^2 \rho u_{rel}^2}{4} \frac{C_D}{C_C} \]  

(2.14)

In this equation \( d_p \) is the particle diameter, \( \rho \) the fluid density, and \( u_{rel} \) the velocity of the particle relative to the fluid velocity. The drag coefficient \( C_D \) is a function of the particle Reynolds number, which has to be recalculated at every point of the particle trajectory. The Cunningham correction factor \( C_C \) corrects for the 'slip' of the fluid directly at the surface of the particle. This correction is necessary for particles of which the size is comparable to the mean free path of the gas molecules (\( \lambda \)), which is a function of temperature and pressure. Although the force experienced by a particle present in the flow field is clearly not stationary, it is assumed to be approximated satisfactorily by Equation 2.14. In the modelling study the particle diameter has been varied from 0.02 \( \mu \)m to 20 \( \mu \)m, the usual range of interest in aerosol technology. Average particle trajectories were calculated for particles seeded at various starting positions, under the assumption that turbulence effects have little influence.

By varying the size of the particles injected in nozzle B, three trajectory regimes can be distinguished (Figure 2.6, next page). Small particles (\( d_p \leq 0.8 \mu \)m) are able to follow the streamlines and leave the nozzle with trajectories which seem to radiate from a source located upstream from the exit plane. Because the particles which are injected close to the nozzle wall have trajectories that fan out at a wide angle, these particles are not transported to the next vacuum chamber. Instead they deposit on the wall around the skimmer. Bigger particles (\( d_p > 0.8 \mu \)m) have more difficulty following the stream lines. At the nozzle exit plane, where the sharpest bend is located, these particles break away from the stream lines, and cross the beam axis. After a short distance the gas density is reduced to such an extent that it no longer influences the particle trajectories. In this regime the particles seem to radiate from a source located just downstream from the nozzle exit plane. Even bigger particles (\( d_p > 2 \mu \)m) are likely to break away from the stream lines before even leaving the nozzle. This causes some of them to impact on the inside wall of the nozzle. The results are summarized in Figure 2.7b, which shows the percentage of particles in each of the three regimes, for particle sizes ranging from 0.02 to 20 \( \mu \)m. The listed values are corrected for the focusing of the particles in the 30 cm tube preceding the nozzle, which is a natural tendency of potential flows (Robinson 1956). This effect has been used by Liu et al. (1993) to produce aerosol beams from small particles (0.01-0.5 \( \mu \)m) with very low divergence angles.
If the same particle size range (0.02-20 μm) is injected in nozzle A, only two trajectory regimes are found. Because the flow channel converges very gradually, the streamlines do not show the sharp bend as with nozzle B. This reduces the number of particles impacting on the skimmer wall, which makes nozzle A more suitable for transporting relatively large particles.

Comparing the results for both geometries (see Figure 2.7, next page), it can be concluded that in both cases the transport efficiency depends on particle size. The size selectivity can be suppressed by restricting the aerosol to the centre part of the nozzle tube, which can be achieved by surrounding it with a sheath of filtered air. This phenomenon has been visualized by Furstennau et al. (1994), who photographed the light scattered by 3 μm polystyrene spheres suspended in a subsonic aerosol jet. The effect of sheath air can be modelled by seeding only the centre part of the flow with particles, thus creating a 'clean zone' around the aerosol.
Figure 2.7 Percentage of particles in each of the three trajectory regimes for nozzle A (top) and B (bottom)
The effect of the magnitude of the sheath air flow on transport efficiency is shown in Figure 2.8. The region with 100% efficiency can be extended from 0.8-1.0 μm to 0.5-2.0 μm, but only when sheath air constitutes 84% of the total flow. This implies that the rate at which particles are transported to the measurement volume would be reduced to approximately 16% of the original value. It is therefore not advisable to apply sheath air when the particle concentration is low.

![Graph showing transmittance vs. particle diameter](image)

Figure 2.8 Influence of the amount of sheath air on the transport efficiency of nozzle B.

In order to rely on the results of the modelling study with Fluent®, a validation is necessary. For every configuration modelled the sample flow rate was calculated and compared with the theoretical value calculated according to the method described in section 2.4.2. As will be shown in section 2.5.2, the theoretical values are in excellent agreement with the measured flow rates. Table 2.2 (next page) shows that the model prediction for the 500 μm nozzle corresponds reasonably well with the theoretical value, but that the agreement is poor for smaller nozzle diameters. This is an indication that wall effects play a significant role. Nevertheless it is assumed that the boundary conditions of the gas flow field are modelled correctly.
Table 2.2 Comparison of sample flow rates for different nozzle diameters. Listed are values from model calculations (section 2.4.2) and results from the Fluent® study.

<table>
<thead>
<tr>
<th>nozzle diameter (μm)</th>
<th>sample flow rate (l/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>model calculations</td>
</tr>
<tr>
<td>200</td>
<td>0.278</td>
</tr>
<tr>
<td>300</td>
<td>0.850</td>
</tr>
<tr>
<td>500</td>
<td>2.360</td>
</tr>
</tbody>
</table>

Additionally the particle terminal velocity was determined for a range of particle sizes. The results are shown in Figure 2.9, together with values from literature (Dahneke 1973, 1974, 1978; Dahneke and Padliya 1977; Prather et al. 1994) and values calculated using an alternative algorithm. For the latter calculations the centreline velocity of the gas was calculated according to equations given by Dahneke (1978), which are also listed in Appendix 2C. The particle motion was calculated using relations describing the drag force, similar to those used in the modelling study.

![Diagram](image)

Figure 2.9 Particle terminal velocity as a function of particle size (axial component). Shown are values from the one-dimensional model described in Appendix 2C, the Fluent study, and various literature sources.
Figure 2.9 shows that there is a significant spread in the terminal velocities from the different sources. The differences are nevertheless not alarming, since the conditions at which the results were obtained are very different and not well characterized. It is a fact that the terminal velocity of a particle is highly dependent on the flow field, which is completely determined by the geometry and dimensions of the nozzle and the system pressures and temperatures.

2.5 Practical performance of the aerosol beam generator

2.5.1 Experimental setup

The optimum parameters determined in section 2.4 have been used to design an experimental setup, schematically shown in Figure 2.10. The sample is drawn into a 20 cm length, 1 cm inner diameter stainless steel tube [1] and transported to the nozzle section. The nozzle [2] can easily be exchanged without influencing the alignment. Both nozzle A and nozzle B, shown in Figure 2.4, have been manufactured and were available in diameters of 0.2 mm (just B), 0.3 mm (just A) and 0.5 mm (both A and B). The aerosol expands into the first vacuum chamber, which is pumped by a 12 m³/hr rotating vacuum pump (Edwards E2M12). The core of the aerosol beam passes through the first skimmer [3], located 4 mm downstream from the nozzle exit. The skimmer is aligned with the nozzle and fixed in position, and its diameter is approximately 0.4 mm. The second vacuum chamber is pumped by a small oil diffusion pump (Edwards EO40/55) with a 2 m³/hr forepump (Edwards E2M2). Finally, the aerosol beam passes through the second skimmer [4], which is 0.3 mm in diameter and located 10 mm downstream from the nozzle. The beam enters the analysis section [5], pumped by a second oil diffusion pump (Edwards Diffstack CR63/150M). As has been shown in Appendix 2A for a 0.5 mm nozzle, this geometry yields an aerosol beam with a maximum diameter of 2 mm at the measurement location. A smaller nozzle diameter would reduce both the diameter and the divergence of the beam.
Figure 2.10 Longitudinal cross section of the aerosol beam generator.
2.5.2 Sample flow rate

The sample flow rate is an important analysis parameter, because it determines the time needed to measure a specific number of particles for a given particle concentration. It is possible to relate the sample flow rate to the nozzle exit diameter, as has been shown earlier (section 2.4.2). In this section the values calculated from flow theory will be compared to those measured experimentally.

Because the nozzles have relatively small diameters, they cannot be manufactured exactly according to specifications. It is therefore necessary to measure the area at the nozzle exit for every single nozzle. This has been done with a microscope connected to an image analysis system (Joyce Loeb Magiscan-2A). From the area an equivalent circle diameter can be calculated. Table 2.3 lists these diameters for all available nozzles, and the sample flow rates calculated assuming $T_0=298$ K. The experimental values were determined with a bubble flow meter (0.1 and 0.2 mm nozzles) and a rotameter (0.3 and 0.5 mm nozzles).

Table 2.3 Calculated and measured sample flow rates for each of the manufactured nozzles.

<table>
<thead>
<tr>
<th>nozzle type</th>
<th>equivalent circle diameter (μm)</th>
<th>sample flow rates (l/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>experimental</td>
</tr>
<tr>
<td>B</td>
<td>121</td>
<td>0.110</td>
</tr>
<tr>
<td>B</td>
<td>224</td>
<td>0.381</td>
</tr>
<tr>
<td>A</td>
<td>307</td>
<td>0.897</td>
</tr>
<tr>
<td>B</td>
<td>499</td>
<td>2.125</td>
</tr>
<tr>
<td>A</td>
<td>532</td>
<td>2.686</td>
</tr>
</tbody>
</table>

Figure 2.11, shown on the next page, gives the sample flow rates in a plot and illustrates that there is a good correlation between calculated and measured values. Furthermore it shows that the flow rates measured with nozzle B are consistently low. Apparently boundary effects do play a role, even though the nozzle Reynolds number is in the range from $2.9\times10^3$ to $1.3\times10^4$. Although the effect is not very strong the results contradict the observations by Ashkenas and Sherman (1966), who reported no influence of boundary layer formation for nozzle Reynolds numbers exceeding 300.
Figure 2.11 Comparison of the measured sample flow rates with the calculations based on the equations in section 2.4.1b.

2.5.3 Ultimate vacuum

As already stated in section 2.3.2 the application of a time-of-flight mass spectrometer implies that the pressure has to be reduced to approximately $10^{-4}$ Pa. The vacuum pumps were chosen as to achieve this pressure when using a 0.2 mm diameter nozzle. It was anticipated that bigger nozzle diameters would yield higher end pressures, but in practice satisfactory vacuum can be achieved with a 0.3 mm nozzle as well. A complete overview of the system pressures for all nozzles available is shown in Table 2.4. It should be noted that it is not possible to use the 0.5 mm nozzle in combination with the tof-ms with the available pumps.
Table 2.4 Pressures measured with the experimental setup for different nozzles

<table>
<thead>
<tr>
<th>nozzle diameter (mm)</th>
<th>Geometry</th>
<th>pressure (Pa) at 1st stage</th>
<th>pressure (Pa) at 2nd stage</th>
<th>pressure (Pa) at 3rd stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>B</td>
<td>$8 \times 10^1$</td>
<td>$1 \times 10^{-2}$</td>
<td>$7 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.3</td>
<td>A</td>
<td>$4 \times 10^2$</td>
<td>$1 \times 10^0$</td>
<td>$3 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.5</td>
<td>A/B</td>
<td>$1 \times 10^3$</td>
<td>$7 \times 10^1$</td>
<td>$5 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

2.5.4 Aerosol beam dimensions

The aerosol beam dimensions must be known if the fraction of particles passing through the measurement volume is to be calculated. Experiments have been performed to verify the modelling results obtained with Fluent®. The diameter of the aerosol beam can only be measured indirectly, for example by collecting the particles on a slide. A special construction was manufactured to place small glass slides (5 mm in cross section) in front of the nozzle at a distance of 4 mm. The construction, shown in Figure 2.12, was connected directly to a rotating vacuum pump in order to achieve the necessary pressure drop.

![Figure 2.12 Schematic representation of the set-up used in the deposition experiments.](image-url)
Monodisperse polystyrene latex (PSL) particles, coloured with a fluorescent dye, were used in all experiments. They were available in diameters of 0.501, 1.01, 2.26, and 2.87 μm (Duke Scientific Corporation). Test aerosols were generated by nebulizing a 0.01 vol% suspension of a PSL sample and removing the water through heating and absorption in silica gel (SiO₂·n H₂O). The particles were collected on thin glass slides, 5 mm in diameter. The slides were treated with a 10% solution of vacuum grease (Apiezon-L) in toluene. This resulted in a coating, which had a thickness in the order of the particle diameter. After the deposition experiment the glass slide was removed from its holder and studied under a microscope. Even submicrometre particles were easy to distinguish from the background with the aid of an ultraviolet lamp in combination with a set of special bandpass filters. The size of the particle deposition, defined as the average of its width and height, was measured with an accuracy of 0.1 mm.

Two deposition experiments were performed with each of the available PSL suspensions. Typically 5 millilitres of a 0.01 vol% concentration suspension were nebulized, which yielded sufficient particles to characterize the depositions by their average diameters. The measured deposition diameters are shown in Figure 2.13, as are the values predicted by the modelling study with Fluent. The graph shows that the measurements display the same trend as the model, but quantitative agreement is poor.

![Graph showing deposition diameters measured and calculated for particles with diameters of 0.501, 1.01, 2.26 and 2.87 μm.](image-url)
It is important to note here that the depositions did not have sharp boundaries, most likely due to particle bounce. Particles were found scattered all over the slide in all experiments, indicating that bounce plays an important role. Dahneke (1973a) has investigated the sticking probabilities of 1.27 μm polystyrene latex spheres striking target surfaces at normal incidence in vacuum. He determined the magnitude of the capture limit velocity \( v^* \) above which bouncing predominates and below which sticking usually occurs, and found 0.83 and 0.91 m/s for polished stainless steel and polished quartz surfaces. Theoretical models (Meteor et al. 1990; Matier and Willeke 1992) predict the critical speed for different particle sizes. For PSL particles on a smooth surfaces the critical speed ranges from 1.5 m/s (\( D_p=0.1 \) μm) to 0.03 m/s (\( D_p=10 \) μm). In the present setup the particles reach a much higher speed, which depends on their size and ranges from roughly 50 m/s to 500 m/s (see also section 2.5.1). The grease coating slows down the particles and increases the capture limit velocity, but apparently this is not sufficient to capture all particles. Some of them still bounce from the surface, after which they can deposit anywhere within the setup. At present, no solution has been found yet to overcome this problem.

### 2.5.5 Transport efficiency

Because the software did not allow for modelling of the complete beam generator, experiments were necessary to obtain information on the overall transport efficiency. For this purpose a monodisperse aerosol was generated, using a vibrating orifice aerosol generator (TSI model 3450). The aerosol was produced from a solution of corn oil in isopropanol, which also contained a fluorescent dye (fluoresceine). The concentration of the aerosol was determined in a separate experiment with an optical particle counter (Climet CI-226M + CI-1000 combination). A more detailed description of the aerosol generation and measurement system can be found in section 3.3.4. Particles were sampled from the aerosol for a fixed time period and deposited on a glass slide placed behind the second skimmer. Because the particles are liquid, the problems with particle bounce described in the previous section are not relevant here. The resulting deposition was studied under a microscope and next washed from the slide using an ultrasonic bath. This method yields a solution of oil and fluorescent dye in isopropanol, and the concentration of the dye can be determined with a fluorometer (Turner model III). A fluorometer is an instrument for measuring the fluorescent activity of a sample, often used in biological applications. It employs the light from a UV-lamp (filtered by a bandpass filter) to excite the fluorescent compound and a photocell (with a second bandpass filter) to measure the emitted fluorescent light. Quantitative determination of the amount of fluorescent tracer enables the calculation of the number of particles deposited on the slide and also the transmission efficiency, provided the initial particle concentration is known.
As the described method is difficult and laborious, it was decided to perform just one experiment to get a rough idea of the transmittance. An aerosol was generated from a solution containing 0.106 vol % corn oil and 4 mg/l fluoresceine. The aerosol fed to the beam generator contained approximately $1.8 \times 10^4$ particles per litre, with a nominal diameter of 4 µm. The glass slide was exposed to the aerosol beam for 60 minutes and microscopic inspection revealed a nice, circular deposition, 0.45 mm in diameter. As the slide was placed 5.2 mm from the second skimmer (0.3 mm in diameter), this result implies that the beam divergence can be characterized by a half angle of 0.83°, equivalent to a solid angle of $6.5 \times 10^{-4}$ sterad. With this result the radius of the aerosol beam at the analysis location can be calculated, and the outcome (0.44 mm) is well within the maximum radius of 1 mm specified in Appendix 2A. The deposited material was dissolved in 10 ml of isopropanol, and a fluorescence intensity of 29 % was measured. From the calibration curve, reproduced in Appendix 2D, this intensity is found to correspond to a fluoresceine concentration of 12 µg/l. The total quantity of fluorescein is therefore $0.12 \, \mu g$, which yields a total volume of corn oil of $3.17 \times 10^{-11} \, m^3$. As the volume of one 4 µm particle is $3.35 \times 10^{-17} \, m^3$, a total number of $9.46 \times 10^5$ particles is estimated to have deposited during the experiment. The aerosol beam generator was equipped with the 0.3 mm convergent nozzle (geometry A), which has a sample flow rate of 0.897 l/min (section 2.5.2). From the sample flow rate, sample time and the initial concentration it can be calculated that approximately $9.69 \times 10^5$ particles have entered the beam generator during the experiment. From this number and the total number of deposited particles ($9.46 \times 10^5$) it follows that the transport efficiency lies within 90 and 100 %. This favourable result agrees with the results from the Fluent® study, described in section 2.4.6.

References


Dahneke, B., J. Hoover and Y.S. Chen (1982).

Similarity theory for aerosol beams, *J. Colloid Interface Sci.* 87, 167-179.


Characteristics of a capillary-generated particle beam, *J. Colloid Interface Sci.* 93, 84-94.

French, J.B. (1865).


High-speed beams of small particles, *J. Colloid Interface Sci.* 24, 330-337.


*Het genereren van deeltjesbundels*, Internal report in Dutch, Delft University of Technology, Delft.


Murphy, W.K. and G.W. Sears (1964).


Shapiro, A.H. (1953).


Appendix 2A Calculation of the skimmer diameter

The figure shown on the right gives a schematic view of the aerosol beam and its divergence. The beam leaves the nozzle with radius $R_N$ and with a maximum divergence angle $\alpha$. The solid angle $\delta$ is related to the divergence angle by the following relation:

$$\delta = 2\pi (1 - \cos \alpha) \quad (2A.1)$$

The skimmer, which has a radius $R_{Sk}$, is located at a distance $x_{Sk}$ from the nozzle exit plane. The measurement volume has a linear dimension of $2R_M$ and is located at a distance $x_M$.

Four parameters have already been chosen: $R_N = 0.25 \text{ mm}$, $x_{Sk} = 10 \text{ mm (4+1+5)}$, $x_M = 30 \text{ mm}$, $R_M = 1 \text{ mm}$

The unknown parameters can be found by solving a set of 3 equations:

$$\frac{R_N}{x_0} = \frac{R_{Sk}}{x_{Sk} - x_0} = \frac{R_M}{x_M - x_0} = \tan \alpha \quad (2A.2)$$

Substitution of the first equation into the third yields $x_0 = 6 \text{ mm}$; inserting this value into the first equation yields $\tan \alpha = 1/24$. This value corresponds to a solid angle $\delta = 5.45 \times 10^{-3} \text{ sterad}$. The second equation can be rewritten to give $R_{Sk}$, and substituting the values found for $x_0$ and $\tan \alpha$ shows that $R_{Sk} = 0.16 \text{ mm}$. The optimal value for the skimmer diameter is therefore $0.32\ (0.3) \text{ mm}$.
Appendix 2B Listing of the user-defined subroutine for calculating the drag coefficient

FUNCTION USERCD( RE, DP, PRESSR, TEMP, VISCOS, + DENSITY, DENP, IVALUE, JVALUE, KVALUE, LVALUE )

NAME : USERCD

PROGRAM : FLUENT

VERSION : V3.03.1 usercd.F 12/13/90

(C) COPYRIGHT BY CREARE.X, INC., 1989
MODIFIED BY OLAF KIEVIT, DEC. 1993

ARGS DESCRIPTION

INPUT : RE - REYNOLDS NUMBER BASED ON PART. DIAM., AND
          THE RELATIVE VELOCITY
DP - PARTICLE/DROPLET DIAMETER
PRESSR - FLUID ABSOLUTE PRESSURE
TEMP - FLUID TEMPERATURE
VISCOS - FLUID MOLECULAR VISCOSITY
DENSITY - FLUID DENSITY
DENP - PARTICLE/DROPLET DENSITY
IVALUE - I-LOCATION OF FLUID CELL
JVALUE - J-LOCATION OF FLUID CELL
KVALUE - K-LOCATION OF FLUID CELL
LVALUE - L-INDEX OF FLUID CELL

OUTPUT : NONE

PURPOSE : THIS FUNCTION COMPUTES THE DRAG COEFFICIENT, CD, FROM
          A USER SUPPLIED FUNCTION

COMMENTS : THE DIAMETER, PRESSURE, TEMPERATURE, VISCOSITY, AND
          DENSITIES ARE IN THE USER SPECIFIED UNITS. THE
          RETURNED VALUE OF CD IS DIMENSIONLESS. THE DRAG
          COEFFICIENT, CD, IS DEFINED FROM :

          DRAG FORCE = (PI*R**2)*(1/2)*(DENSITY*U**2)*CD

          WHERE : R = PARTICLE/DROPLET RADIUS
                   DENSITY = FLUID DENSITY
                     U = RELATIVE VELOCITY

CALLED BY : TRACK

FUNCTION TYPE DECLARATION...

REAL USERCD

ARGUMENT TYPE DECLARATIONS...

INTEGER IVALUE
INTEGER JVALUE
INTEGER KVALUE
INTEGER LVALUE

REAL RE
REAL DP
REAL PRESSR
REAL TEMP
REAL VISCOS
REAL DENSITY
REAL DENP
LOCAL VARIABLE TYPE DECLARATIONS...

REAL CC
REAL CW
REAL LAMBDA

BEGIN FUNCTION USERCN...

RELATION FOR VERY SMALL PARTICLES AND/OR LOW PressURES
USING MULTIPLE DRAG FORCE RELATIONS FOR DIFFERENT REYNOLDS
REGIMES, AND CUNNINGHAMS SLIP CORRECTION FACTOR

IF (RE.LE.0.1) THEN
   CW=(24/RE)
ELSEIF (RE.LE.1) THEN
   CW=(22.73/RE)+(0.0903/(RE*RE))+3.69
ELSEIF (RE.LE.10) THEN
   CW=(29.1667/RE)-(3.8889/(RE*RE))+1.222
ELSEIF (RE.LE.100) THEN
   CW=(46.4/RE)-(116.667/(RE*RE))+0.61667
ELSEIF (RE.LE.1000) THEN
   CW=(98.33/RE)-(2738/(RE*RE))+0.3644
ELSEIF (RE.GT.1000) THEN
   CW=(21/RE)+(6./SQRT(RE))+0.28
ENDIF

LAMBDA=2.27E-5*TEMP/PRESS
CC=1.0+2.492*(LAMBDA/DP)+
    + 0.84*(LAMBDA/DP)*EXP(-0.435*(DP/LAMBDA))

USERCN=CW/CC

END FUNCTION USERCN AND RETURN...

RETURN
END
Appendix 2C Calculation of the axial flow field

The following derivation continues where section 2.4.2 left off, yielding centreline results, only valid for ideal gas behaviour and isentropic, frictionless flow. It is derived from several literature sources, including Shapiro (1953), Ashkenas and Sherman (1966) and Dahneke (1978).

It is possible to relate the area $A$ at any point within the nozzle to the Mach number with a relation, similar to Equations 2.11 to 2.13. In this case it is not convenient to refer to the stagnation condition, since the stagnation velocity is zero, and the area is infinite. The nozzle exit, where $M=1$ and $A=A^*$, is therefore a better reference plane.

$$\frac{A}{A^*} = \frac{1}{M} \left[ \frac{\gamma - 1}{2} \frac{M^2}{\gamma + 1} \right]^{(\gamma + 1)/(2(\gamma - 1))} \quad (2C.1)$$

With this equation the Mach number can be calculated for distances $x/D \leq 0$.

For the region near the nozzle where the flow becomes supersonic there is no gas dynamics solution available. However, the flow can be described as a free-jet, when the downstream distance from the nozzle exit $x$ is large enough as compared to the nozzle exit diameter $D$. Dahneke (1978) has proposed a fitting formula for the transition region, based on the numerical data calculated by French (1965), using the method of characteristics. This expression must be consistent with the boundary condition $M=1$ at $x=0$, and with the free-jet behaviour when $x/D$ is large (in this case $x/D=6$). The centreline Mach number can be written as

$$M = 1.0 + \frac{A'x}{D} - B' \left( \frac{x}{D} \right)^{\frac{5}{7}} \quad (2C.2)$$

When the expanding gas is air ($\gamma = 7/5$), the fit parameters $A'$ and $B'$ are 1.55 and 0.042 respectively. The equation holds within the range $0 < x/D < 6$.

At a certain distance from the nozzle exit plane ($x/D=6$) the flow pattern becomes independent from the initial expansion phase. At this point the flow can be described as a free jet, which shows a strong resemblance to a simple source flow. The streamlines seem to radiate from a source, located at a distance $x_0$ downstream from the nozzle. Ashkenas and Sherman (1966) give a fitting formula for the centreline Mach number where $A''$ and $x_0$ are constants. This equation holds for $x/D > 6$, up to the point where the Mach disk is formed. It is possible to extend the application range of Equation 2C.3 to smaller values of $x/D$ by adding a third term.

40
\[ M = A'' \left( \frac{x-x_0}{D} \right)^{\gamma^{-1}} - \frac{1}{2} \frac{\gamma+1}{\gamma-1} \left( \frac{x-x_0}{D} \right)^{\gamma^{-1}} \]  

\[ M = A'' \left( \frac{x-x_0}{D} \right)^{\gamma^{-1}} - \frac{1}{2} \frac{\gamma+1}{\gamma-1} \left( \frac{x-x_0}{D} \right)^{\gamma^{-1}} + C'' \left( \frac{x-x_0}{D} \right)^{3(\gamma^{-1})} \]  

(2C.3)  

(2C.4)

Although the validity is extended down to \( x/D = 1 \), it is uncertain whether this term is analytically correct. For air jets \( \gamma = 1.40 \), \( x/D = 0.40 \), \( A'' = 3.65 \) and \( C'' = 0.20 \). Equation 2C.3 reproduces the results from the method of characteristics approach with an accuracy of about 0.5%.

The free jet region is enclosed by a barrel shock. The position of the Mach disk is only a function of the pressure ratio, and Dupeyrat (1981) derived

\[ \frac{x_M}{D} = 0.65 \left( \frac{p_0}{p_b} \right)^{0.50} \]  

(2C.5)

As described in section 2.4.3, experimental studies have confirmed the suggested relation, although slightly different values were found for the two constants. At distances exceeding \( x_M \) the gas velocity is ill defined, and can no longer be calculated.

With the equations given in the preceding part, combined with a general drag force relation, the speed of a particle travelling on the central axis can be calculated. The particle motion can be described by the following differential equation

\[ \frac{dv_p}{dt} = -\frac{3C_D \rho}{4C_c d \rho_p} |v_p - v| \left( v_p - v \right) \]  

(2C.6)

with \( d \) representing the particle diameter, and the subscript \( p \) denoting particle properties. The drag coefficient \( (C_D) \) is a function of the particle Reynolds number. The Cunningham correction factor \( (C_c) \) has been calculated using Millikan’s expression (1923), with particle size and the mean free path of the gas molecules \( (\lambda) \) as variables. Both the drag
coefficient and the Cunningham correction factor are dependent on flow parameters, and should be recalculated at every point in the flow field. The calculations have been performed for unit density spheres, using a fifth order Runge-Kutta algorithm with a self-adjusting step size. A convergent nozzle geometry was adopted.

After a certain distance, dominated by inertia effects, the particle velocity approaches a constant value: the terminal velocity. It is possible to relate this velocity to the aerodynamic diameter of the particle. In order to get a good correlation the particle shape and density, as well as the gas composition and pressure must be known. The modelling results for unit density spheres have been fitted to yield the particle terminal velocity \( (v_p) \) as a function of size \( (d_p \text{ in } \mu m) \):

\[
\log(v_p) = 2.358 - 0.4361 \times \log(d_p) - 0.08677 \times \log^2(d_p)
\]

(2C.7)

It must be stressed here that the particle velocity is highly dependent on the system configuration, as can be concluded from Figure 2.9.
Appendix 2D Calibration curve for the fluorescence measurements

The measurements have been fitted with a linear function through the origin, and a slope of 2.45 (±0.11) % / μg/l was found. The calibration is only valid when using the filters 430-470 nm and 470-3000 nm for selection of the excitation and fluorescent wavelengths respectively. Furthermore the diaphragm should be set in the '30x' position.
Detection and sizing

3.1 Introduction

This section will address the detection of a particle in the aerosol beam using light scattering and the estimation of its size. Rapid detection is essential for the chemical analysis. If the particles are to be hit by the ionization laser pulse, exact knowledge of their position at a certain moment in time is required. It is also worthwhile to measure the size of the particle, since it is related to its origin and history. Additionally, it determines the dynamic behaviour of the particle, which is linked to things like aerosol stability and respirability. Furthermore it is expected that particle size also influences the chemical analysis by laser-ionization mass spectrometry, as discussed in chapters 4 and 5. In conclusion it can be said that size is one of the most important parameters characterizing a particle.

As already mentioned, rapid particle detection is required if the chemical analysis is to be performed on-line. Furthermore the detection technique has to be non-invasive, since the particles are to be analyzed chemically as well. This makes the use of conventional particle sizers like cascade impactors and aerosol centrifuges impossible. An alternative method for measuring particle size is employed in electrical mobility analyzers. The particle is given a known electrical charge and its deflection in an electric field is measured. Although this method has been applied to naturally charged particles suspended in an aerosol beam (Seapan et al. 1982), it has been rejected because of the problems associated with the high particle speed. Moreover, this technique is difficult to combine with the chemical analysis by laser-ionization mass spectrometry.

The only realistic alternative is to measure the velocity of the particle, which is related to its aerodynamic diameter. The particle velocity can be calculated from the time which elapses when a particle traverses a known, fixed distance: the time of flight (tof). Seapan et al. (1982) have measured flight times by simultaneously chopping the aerosol beam and a light beam placed in parallel. The flight time is found from the delay between the signal from a particle detector, a resistively heated rhenium filament, and a photodiode which measures the light pulses. In practice it is more convenient to use light scattering for measuring the time of flight, as shown in Figure 3.1 on the next page. This concept was developed by Dahneke and coworkers (see e.g. Dahneke and Flachsbart 1972) and used in commercial instruments like the APS 33B Aerodynamic Particle Sizer from TSI and the API Aerosizer from Malvern. Sinha (1984) and Prather
et al. (1994) have successfully applied it in combination with a chemical characterization technique. The method has the advantage that it is almost independent of the optical properties of the particles. The measured diameter is however a function of particle shape and density, and of composition, temperature and pressure of the suspending gas (Cheng et al. 1993). Furthermore the method is known to suffer from coincidence and phantom effects (Heitbrink et al. 1991), which cause sizing errors. Since alignment of the laser and particle beams is critical as well, it was decided to use single particle light scattering in stead.

Figure 3.1 Schematic representation of a setup for measuring the aerodynamic diameter of a particle using light scattering.

Recent developments in phase Doppler instrumentation have made this technique into an interesting option for single particle sizing. The technique uses the spatial and temporal frequency of the Doppler-shifted light, scattered by a particle crossing two interfering laser beams. The measured quantities do not depend on the intensity of the scattered light, which could be a major advantage for our application (see also section 3.5). Although the lower particle size limit was generally accepted to be 2-5 μm, Von Benzor and Buchhave (1994) claim to have measured particles down to 200 nm. These properties make it worthwhile to consider phase Doppler techniques for future work. Unfortunately, the combined information on size and velocity can only be obtained with spherical, transparent particles.
3.2 Theory of light scattering

3.2.1 The physics of light scattering

This section will give a short phenomenological description of light scattering. The following sections will deal with the mathematics of the problem and solutions for spherical particles of different sizes. For a more extensive treatment of this subject the reader is referred to textbooks by Van de Hulst (1957), Kerker (1969) and Bohren and Huffman (1983).

If a particle is illuminated by an electromagnetic wave, electric charges (dipole elements) inside the particle are set into oscillatory motion by the electrical field of the wave. The dipoles oscillate at the frequency of the applied field and secondary radiation is scattered in all directions. Additionally, the excited dipoles can absorb part of the incident electromagnetic energy, converting it into other forms of energy like heat. The total scattered field in a specific direction can be found by superimposing the contributions from the separate dipoles, where the phase differences have to be taken into account. Because the phase relations vary for different directions, the scattered field varies as well. These variations are strongest when the particle is big compared with the wavelength, as will be shown in section 3.2.3. If shape effects are ignored, the scattering behaviour of a particle is dominated by two parameters. The first is the size parameter \( \alpha \), which depends on the particle size \( d_p \) and the wavelength of the incident radiation \( \lambda \)

\[
\alpha = \frac{\pi d_p}{\lambda} \quad (3.1)
\]

The second parameter is the complex index of refraction \( N \), of which the imaginary part \( k \) is a measure for the absorption of radiation.

\[
N = n + ik \quad (3.2)
\]

In general, the refractive index depends on temperature and on the wavelength of the radiation.

3.2.2 Light scattering by a sphere: Mie theory

A theoretical description of the process of light scattering by a particle involves examining how the electromagnetic field is disturbed by an obstacle. Every solution to this problem must satisfy the Maxwell equations, both inside and outside the particle. As can be derived (see e.g. Bohren and Huffman 1983), the relation between incident and scattered fields can be described by the amplitude scattering matrix, of which the elements depend on the scattering angle. It is convenient to use the Stokes parameters, \( I \), \( Q \), \( U \) and \( V \), to characterize the fields. \( I \) represents the intensity of the light, and \( Q \), \( U \), and \( V \) describe the state of polarization.
The relationship between the incident and scattered Stokes parameters is:

\[
\begin{bmatrix}
I_s \\
Q_s \\
U_s \\
V_s
\end{bmatrix} = \frac{1}{k^2 r^2}
\begin{bmatrix}
S_{11} & S_{12} & 0 & 0 \\
S_{12} & S_{11} & 0 & 0 \\
0 & 0 & S_{33} & S_{34} \\
0 & 0 & -S_{34} & S_{33}
\end{bmatrix}
\begin{bmatrix}
I_i \\
Q_i \\
U_i \\
V_i
\end{bmatrix}
\] (3.3)

In this equation \( r \) is the distance from the scattering source, and \( k \) is the wave number, which is a function of the refraction index of the medium surrounding the particle \( (N_2) \) and the wavelength of the incident light:

\[
k = \frac{2\pi N_2}{\lambda}
\] (3.4)

From Equation 3.3 it is clear that the theoretical description of light scattering by an irregularly shaped particle in an arbitrary radiation field is very complex. Therefore the remainder of this section will consider spherical particles, staying close to the derivations given by Bohren and Huffman (1983).

If the particle in question is an optically homogeneous sphere the scattering problem can be solved by what is generally known as Mie theory. Because of the symmetry involved, the scattering matrix can be simplified considerably:

\[
\begin{bmatrix}
I_s \\
Q_s \\
U_s \\
V_s
\end{bmatrix} = \frac{1}{k^2 r^2}
\begin{bmatrix}
S_{11} & S_{12} & 0 & 0 \\
S_{12} & S_{11} & 0 & 0 \\
0 & 0 & S_{33} & S_{34} \\
0 & 0 & -S_{34} & S_{33}
\end{bmatrix}
\begin{bmatrix}
I_i \\
Q_i \\
U_i \\
V_i
\end{bmatrix}
\] (3.5)

with

\[
S_{11} = \frac{1}{2}(|S_2|^2 + |S_1|^2)
\] (3.6)

\[
S_{12} = \frac{1}{2}(|S_2|^2 - |S_1|^2)
\] (3.7)

\[
S_{33} = \frac{1}{2}(|S_2 S_1 + S_2 S_1^*|)
\] (3.8)

\[
S_{34} = \frac{i}{2}(|S_2 S_1^* - S_2 S_1|)
\] (3.9)
The elements of the amplitude scattering matrix can be calculated with the following expressions, truncated at $n$ terms:

$$S_1 = \sum_n \frac{2n+1}{n(n+1)} (a_n \tau_n + b_n \pi_n)$$  \hspace{1cm} (3.10)

$$S_2 = \sum_n \frac{2n+1}{n(n+1)} (a_n \tau_n + b_n \pi_n)$$  \hspace{1cm} (3.11)

In these equations $a_n$ and $b_n$ are the scattering coefficients, which are functions of the size parameter and refractive index. $\tau_n$ and $\pi_n$ are angle-dependent functions, especially defined to facilitate computation of the amplitude scattering matrix. The most interesting Stokes parameter for our purpose is $I$, which represents the intensity of the radiation (irradiance). The intensities of the incident light and the light scattered at an angle $\theta$ are in general related through the parameters $S_{11}$ and $S_{12}$, and when the incident light is polarized parallel to the scattering plane the relation is:

$$I_s = \frac{1}{k^2 r^2} (S_{11} + S_{12}) I_i$$  \hspace{1cm} (3.12)

In case the incident light is polarized perpendicular to the scattering plane, the following relation holds:

$$I_s = \frac{1}{k^2 r^2} (S_{11} - S_{12}) I_i$$  \hspace{1cm} (3.13)

If the incident light is unpolarized the scattering intensity is the average of Equations 3.12 and 3.13, and thus only dependent on $S_{12}$.

### 3.2.3 Limitations of Mie theory and alternative theories

In the present work the light scattered by a particle in the aerosol beam is modelled with Mie theory. In general, Mie theory can be used to calculate scattering intensities at arbitrary angles and size parameters, provided the particles are homogeneous and spherical. For particles much smaller than the wavelength ($\alpha << 1$), which also satisfy the condition

$$\frac{N_{\text{particle}}}{N_{\text{medium}}} \alpha << 1$$  \hspace{1cm} (3.14)

light scattering becomes more and more a volume effect. This implies that the amount of light scattered at a specific angle is primarily a function of the volume of the particle, regardless of its shape (Gebhart 1976). For these small particles Rayleigh developed a theory, which can be considered a simplified version of Mie theory.
In this case the elements of the amplitude scattering matrix can be calculated from
\[
S_1 = \frac{-ik^3 \alpha}{4\pi} \tag{3.15}
\]
and
\[
S_2 = \frac{-ik^3 \alpha}{4\pi} \cos \theta \tag{3.16}
\]
This yields angular scattering patterns which are relatively simple and symmetrical, as can be seen from Figure 3.2a. The parameter $S_{11}$ is plotted on a logarithmic scale, using software developed at the Delft University of Technology (see e.g. Boxman et al. 1991).

Figure 3.2 Polar scattering plots calculated with MIE4X4S for $\lambda=633$ nm and particle diameters of 0.5 (a), 1 (b), 2 (c) and 6 μm (d). The parameter $S_{11}$ is plotted, on a logarithmic scale.
If the particles are large in comparison with the wavelength (α>1) concepts from geometrical optics can be used to describe their scattering. This is for instance the case when the sun illuminates water droplets and creates a rainbow. In the geometrical optics approach it is assumed that the incident plane wave can be subdivided into a large number of rays, which behave according to the Fresnel equations and Snell’s law. The resulting scattering pattern (see Figure 3.2 c and d) shows a great number of minima and maxima and most of the incident light is scattered in the forward direction. Although the calculation schemes are relatively simple for the geometrical optics approximation, the results are in good agreement with Mie theory.

By applying Mie theory in the calculation of scattered light distributions, a number of assumptions are made. Firstly it is assumed that the particles are spherical. Although in the present study all experiments were performed with either liquid or polystyrene latex particles which can be considered spherical, this will in general not be the case. Secondly it is assumed that the particles are optically homogeneous and that the index of refraction is known. This is true for the test aerosols used in the present study, but for ‘real life’ aerosols the optical properties are often unknown and inhomogeneous. Thirdly Mie theory relies on the assumption that the incident radiation can be considered a plane wave. In general this will not be the case, and Gouesbet and coworkers developed a theory to account for this (Gouesbet et al. 1988, Maheu et al. 1988, Ren et al. 1994). With this theory, called generalized Lorenz-Mie theory (GLMT), it is possible to describe scattering by a particle located anywhere within a beam with an arbitrary intensity distribution. However, the theory requires coefficients which describe the electrical and magnetic wavefront as the sum of a series of plane waves. In practice these coefficients are difficult to obtain, which makes GLMT at present unsuitable for routine applications.

It is important to note that Mie theory introduces errors, because in reality the laser radiation is not a plane wave. The intensity profile encountered in experimental setups causes what is known as the intensity (sizing) ambiguity problem. The scattering signal is not readily interpretable, since it is not just a function of the size, shape and optical properties of the particle, but also of its trajectory. Signals from large particles passing through the edges of the laser beam cannot be distinguished from small particles passing through the centre of the beam. Holme and Self (1979) developed an inversion procedure which corrects scattered light data for particle trajectory effects, through calibration with monodisperse aerosols. Unfortunately, this procedure can only be applied to an ensemble of particles, which makes it unsuitable for single particle characterization.
3.3 Light scattering experiments

3.3.1 Choice of components

A single particle light scattering setup basically consists of a light source, a light trap, optics to guide the light and one or more detector(s). The light source can be either a lamp or a laser. A lamp has the advantage that it emits over a wide spectral range, causing the light to be polychromatic. Because of the averaging over the spectral range of the lamp, the response curve, which gives the scattered light intensity as a function of particle size, displays less oscillations than for monochromatic radiation. In practice the spectral range cannot be exploited to full extent, because optical filtering is necessary to protect the detectors from the pulsed laser radiation. A disadvantage is that a lamp can be considered an imperfect point source, which limits the extent to which the light can be focused. In contrast, a laser produces a narrow beam which can be focused down to a spot size in the order of a micrometer. This implies that much higher intensities can be reached, which makes lasers especially suitable for applications like light scattering (Hecht 1986). Because laser radiation is in general monochromatic the problem of the oscillating response curve has to be dealt with. This problem can be avoided by using a lamp, or a laser with multiple wavelengths (Van der Meulen and Strackee 1979).

In the present setup a 16 mW multimode helium-neon laser is employed (Melles Griot model 05-LHR-981, wavelength 632.8 nm). It was selected because of its compactness, low price and relatively high output power. Higher power lasers, either helium-neon, argon-ion or other types, are both bigger and much more expensive. The multimode character of the laser effects the intensity profile of the beam, which results from superimposing the profiles of the separate TEM-modes. The profile, shown as Figure 3.3 on the next page, resembles a Gaussian, but is somewhat flatter causing it to look more like a so-called top-hat profile. The intensity dip in the centre of the beam is characteristic, but not very important because of the small fraction of the total area it occupies. The radiation is randomly polarized, which implies that the beam appears to be unpolarized when integrating over a fairly short period of time.

The laser beam is focused in the centre of the analysis section with a two lens system. Using two lenses instead of one makes the spot size up to ten times smaller, resulting in an increase in intensity with a factor 100. Gaussian beam theory and geometrical optics are combined to construct a so-called ABCD law for a Gaussian wave (see e.g. Guenther 1990), and a complete derivation can be found in Appendix 3A. The ABCD law enables calculation of the beam waist, i.e. the half-width at an amplitude equal to 1/e of the maximum amplitude of the wave, at any location on the optical axis. As the appendix shows, the focal radius (the minimum beam waist) is calculated to be 8.2 μm. In reality the focus is significantly bigger because of the multimode character of the laser.
Figure 3.3 Measured intensity profile for the unfocused multi-mode helium-neon laser.

There are two types of detectors available for measuring low level light signals: solid-state detectors (photodiodes) and photomultiplier tubes (PMT's). Both detector types are sensitive to the wavelength of a helium-neon laser (632.8 nm) and thus equally suitable. There are differences though, which are summarized in Table 3.1.

Table 3.1 Characteristics of avalanche photodiodes and photomultiplier tubes (Burle 1980).

<table>
<thead>
<tr>
<th>characteristic quantity</th>
<th>avalanche photodiode</th>
<th>photomultiplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>speed of response</td>
<td>10-20 ns</td>
<td>2 ns</td>
</tr>
<tr>
<td>gain</td>
<td>100</td>
<td>$10^3$-$10^8$</td>
</tr>
<tr>
<td>sensitive area</td>
<td>0.5 mm$^2$</td>
<td>up to 100 cm$^2$</td>
</tr>
<tr>
<td>Noise Equivalent Power</td>
<td>$10^{-13}$ W</td>
<td>$10^{-16}$ W</td>
</tr>
<tr>
<td>(S/N ratio)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>coupling resistor</td>
<td>5 MΩ</td>
<td>50 Ω</td>
</tr>
</tbody>
</table>

The table shows that photomultipliers are the best choice for the present application. Taking all specifications into account, a PMT of type 9202B with a type A1 transimpedance amplifier (THORN EMI Electron Tubes, UK) was selected. Two long wave pass filters (Schott type OG 570) were installed to avoid damage by the vaporization/ionization laser pulses.
Every photomultiplier suffers from dark current: a signal which is produced when there is no light present. Dark current in a photomultiplier tube may be categorized by origin into three types: ohmic leakage, thermionic emission of electrons and regenerative effects. Ohmic leakage results from the imperfect insulating properties of the glass stem or plastic base. This type of leakage is usually negligible, except in situations where condensation is likely to occur. At higher voltages, ohmic leakage is obscured by other sources of dark current. Thermionic emission of electrons, primarily from the photocathode, causes pulse-shaped signals which are sometimes called dark spikes. This type of dark current increases with the applied voltage, and it can be reduced by cooling. Each emitted electron results in an output pulse having a magnitude equal to one or more elementary charges, multiplied by the gain of the tube. Regenerative effects, such as ionic bombardment of the photocathode, typically cause pulses corresponding to multiple charges. Other mechanisms contributing to the noise spectrum include cosmic rays, field emission and scintillation of the glass envelope.

3.3.2 The experimental setup

When the aerosol beam generator was designed, the geometry of the ion optics was already given by the manufacturer of the time-of-flight mass spectrometer. Figure 3.4 gives a top view of the ion optics, which will be explained in detail in section 5.3. The back electrode and first grid are positioned right next to the aerosol beam, which reduces the possibilities for placing the light scattering equipment to the locations marked 1 to 5. The centre line, passing through 1 and 5, was chosen as the primary beam axis. This has the advantage that the optical axis is perpendicular to both the aerosol beam and the primary axis of the time-of-flight mass spectrometer. Therefore, the influence from one part of the setup to any other part is minimized. Having made this decision only the locations 2, 3 and 4 are available for positioning the detector(s).

![Figure 3.4](image)

Figure 3.4 Top view of the analysis section. The letters a, b and c indicate the back electrode, first grid and second grid respectively. * indicates the position of the aerosol beam.
Preliminary experiments had already shown that multiple detectors are necessary to make the setup work satisfactory. If only one detector is used, false triggers are generated whenever a dark spike occurs. Furthermore particle sizing is impossible because of the intensity ambiguity problem discussed in section 3.2.3. A second detector yields additional information, which can be used to estimate the size of the particles.

Of all locations available the numbers 3 and 4 are most suitable for scattered light detection. At location 2 only back-scattered light can be collected which has a low intensity as compared to light scattered in the 90° or forward direction, especially for big particles (d>λ). This difference is illustrated by Figure 3.2, which shows scattering patterns for particles with a diameter of 0.5, 1, 2 and 6 micrometer. Please note that the scattering intensity, expressed by the parameter S11, is shown on a logarithmic scale. A multiple ratio single-particle counter (MRSPC) using the same concept, was built and tested by Hirleman and Moon (1982). In their study they considered scattering angles of 48°, 24°, 12°, 6°, 3°, 1°, 0.5° and 0.25°, and calculated response functions for each angle pair. In practice, the instrument sizes a particle using the scattering ratio measured with the largest angle pair which indicates a size consistent with that determined by all smaller angle pairs. In our case we can only measure at two fixed angles, 45° and 90°. This choice is conform observations by Ohigashi et al. (1994), who state that the amount of information is highest when forward and side scattering angles are used in combination. In order to compensate for the difference in signal level between the detectors at 45 and 90° it was decided to use a lens to collect more light at the 90° angle. By increasing the collection angle from 7.59° (no lens) to 15° (with a 60 mm focal length 30 mm diameter lens placed at 56 mm), the signal was improved by a factor of 3 to 4. Figure 3.5 shows the complete optical setup as it was built in practice.

![Figure 3.5 Schematic representation of the complete light scattering setup.](image-url)
3.3.3 Data collection and storage.

The transimpedance amplifiers connected to each of the photomultipliers produce signals in the range from 1 to 200 millivolts for the particle size range of interest ($d_p < 10 \mu m$). In order to shift the signal to a range where the processing equipment has its optimal accuracy additional amplification electronics with a high bandwidth (150 MHz) were employed, multiplying the signal approximately 33 times. For each of the amplified signals a reference voltage is set, to a threshold value just above the noise level. The signals are continuously compared with the reference voltages, and a trigger pulse is generated only when both channels exceed their voltage thresholds. By application of this coincidence filter false triggers through dark spikes are effectively avoided. A more extensive description of the electronics is given in section 4.2.2, which describes how the vaporization/ionization laser is fired. The pulse generated through the coincidence process triggers a 350 MHz bandwidth digital oscilloscope (LeCroy model 9314M), which stores the signals with a sampling frequency of 100 megasamples per second. The application of a pre-trigger delay ensures that the complete scattering peaks are recorded, including the part preceding the trigger pulse. Once the signals have been recorded by the oscilloscope they can be sent to a personal computer via a GPIB interface. This interface is programmable using the standard IEEE protocol. Martin Weiß developed a software package called READWAVE, which fully automatically reads the data (waveform) from the scope and writes it to the computer hard disk. It displays the signals in real time and it contains a number of pre-processing steps like fast Fourier transformation. The light scattering signals were stored without any pre-treatment and processing was done later as a batch process.

3.3.4 Experimental procedure

Two different aerosol generation systems were used to produce the test aerosols for the light scattering experiments. The smallest particles (polystyrene spheres, 0.364, 0.501, 1.01, 2.26 and 3.09 \mu m in diameter from Duke Scientific Corporation, and 1 \mu m from the Technical University of Eindhoven) were dispersed with a DeVilbiss nebulizer. This generation method has also been used in the deposition experiments described in section 2.5.4. The bigger particles (1, 2, 4 and 6 \mu m in diameter) were produced with a vibrating orifice aerosol generator (TSI model 3450). A 20 \mu m orifice was used in all experiments, and the different particle sizes were obtained by varying the concentration of the solute. Corn oil was selected as the solute because it has a very low vapour pressure, which is comparable to that of dioctylphthalate (DOP). Unlike DOP, corn oil is non-toxic and cheap, as it is commercially sold as a food compound. Solutions of corn oil in isopropyl alcohol were sprayed at a liquid feed rate of 0.139 cm$^3$/min and at a frequency of approximately 70 kHz. The size of the produced droplets can be calculated with the well-known equation from Berglund and Liu (1973):
\[ D_s = \left( \frac{6Q}{\pi f} \right)^{\frac{1}{3}} \]  \quad (3.17)

in which \( Q \) is the liquid feed rate and \( f \) the ultrasonic frequency. The droplets are dried in a drying column, which allows the solvent to evaporate. The highly volatile solvent and the high flow rate of the dilution air (50 l/min) guarantee complete drying of the aerosol. The diameter of the resulting aerosol particles can be calculated by multiplying the primary drop volume with the volumetric concentration of the solute, if necessary increased with the concentration of nonvolatile impurities. The concentrations of the solutions used in the experiments are listed in Table 3.2, together with the resulting particle sizes.

Table 3.2 Concentrations of the solutions sprayed with the vibrating orifice aerosol generator and the resulting particle sizes.

<table>
<thead>
<tr>
<th>volumetric corn oil concentration (%)</th>
<th>nominal diameter of the dry particles (( \mu m ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.65\times10^{-3}</td>
<td>1</td>
</tr>
<tr>
<td>1.32\times10^{-2}</td>
<td>2</td>
</tr>
<tr>
<td>1.06\times10^{-1}</td>
<td>4</td>
</tr>
<tr>
<td>3.56\times10^{-1}</td>
<td>6</td>
</tr>
</tbody>
</table>

The size distributions and concentrations of the test aerosols were measured with an optical particle counter (Climet Ci-226M + Ci-1000 combination). The sample flow rate of this instrument is 0.1 cubic foot per minute, and the sampling time was set to 332 seconds (measured volume = 10 litres). The data from the optical particle sizer were down-loaded to a personal computer, and a typical example of a (number averaged) size distribution is shown in Figure 3.6 (next page). It is clear that some coalescence occurs. The dominating peak at 3.7 \( \mu m \) represents the primary particles and multiplets are visible at higher diameters. However, as the number of multiplets constitutes maximally 4% of the total, this effect is not significant for the present study. The primary particle peak has an average of 3.708 \( \mu m \) and a standard deviation of 0.003 \( \mu m \). From the operating parameters of the vibrating orifice aerosol generator and the concentration of the solution a diameter of 4 \( \mu m \) was expected, with an estimated standard deviation of a few percent. The observed deviation is too big to result from the difference in refractive index. It is most likely caused by the optical particle sizer, which is no longer sizing according to its calibration curve. This was confirmed by independent experiments with monodisperse latex samples. It was found that the instrument undersizes 3.09 \( \mu m \) PSL particles by approximately 7.4%, which indicates that our corn oil particles are most likely 4.00 \( \mu m \) in diameter. Similar results were found for all other solutions and therefore particle diameters were calculated using Equation 3.17 and the concentrations of the solutions, with an accuracy of approximately 1%. 

57
3.4 Model predictions and interpretation of the experimental results

3.4.1 Model description

Before analysing the experimental results it is worthwhile to look at the response expected from the light scattering experiments. A set of simple models suffices to predict the response, thus aiding in the interpretation of the results and the realization of the final target: obtaining a reliable estimate for the size of single particles.

The ABCD law described in Appendix 3A not only estimates the focal size, it also yields a general expression for the beam waist as a function of the axial distance z (Equation 3A.15). If this expression is combined with a description of the radial intensity profile it is possible to construct a function which predicts the intensity at any point within the laser beam. In order to achieve this the measured radial intensity profile, shown in Figure 3.3, has been fitted with a function

\[
I(r) = \frac{h_1}{1 + \exp \left( \frac{r - d_1}{s_1} \right)} + \frac{h_2}{1 + \exp \left( \frac{r - d_2}{s_2} \right)}
\]  

(3.18)
The values of the coefficients in this equation were determined through a least-squares fit. Equations 3.18 and 3A.15 can be combined by making the coefficients a function of the axial coordinate:

\[ h_1 = 7.7 \times 10^7 \, \text{W/m}^2 \times (w(0)/w(z))^2 \]

\[ h_2 = 9.5 \times 10^6 \, \text{W/m}^2 \times (w(0)/w(z))^2 \]

\[ d_1 = 7.71 \times 10^{-6} \, \text{m} \times w(z)/w(0) \]

\[ d_2 = 2.8 \times 10^{-6} \, \text{m} \times w(z)/w(0) \]

\[ s_1 = 1.33 \times 10^{-6} \, \text{m} \times w(z)/w(0) \]

\[ s_2 = 2.9 \times 10^{-7} \, \text{m} \times w(z)/w(0) \]

A surface plot of the resulting function \( I_{3D} \) is shown below (Figure 3.7). The integral of the function over its surface perpendicular to the optical axis should always yield the same value, independent of the axial coordinate. This is confirmed by the approximated analytical solution for \( \sigma d \), obtained using Sommerfeld's lemma (Pathria 1988):

\[
\int_0 I_{3D}(z,r)2\pi r dr = \pi (h_1 d_1^2 + h_2 d_2^2) + \frac{\pi^3}{3} (h_1 s_1^2 + h_2 s_2^2)
\]

(3.19)

Figure 3.7 Surface plot of the function describing both the axial and radial intensity distribution of the focused helium-neon laser beam.

As already mentioned in section 3.2.3, Mie theory was adopted for calculation of the scattered light intensity as a function of the scattering angle. The wide range of intensities makes the integration of the amount of scattered light over the collection angle into a difficult task. Peter Verheijen developed a computer program for this purpose, which we tested using analytical solutions and experimental data. The program is capable of solving the Mie equations for a given case and integrating the scattering intensity over a cone of arbitrary half angle at any angle from the optical axis.
Calculations were performed for polystyrene latex ($N=1.587+0i$) and corn oil ($N=1.473+0i$) particles, in the range from 0.1 to 10 micrometres. The refractive index of corn oil was measured using a refractometer (real part) and a spectrophotometer (imaginary part), and the polystyrene latex value was taken from De Leeuw (1982). The response curves are shown on the next page, as Figure 3.8. As was to be expected, the difference in refractive index causes a small shift in the location and amplitude of the oscillations, which are most profound for transparent materials.

The power of the scattered light calculated in the previous section is measured by the photomultiplier tubes (PMTs), which convert it into an electrical current. Although the manufacturer supplies all PMTs with some data characterizing this conversion it is best to perform an experimental calibration. For this purpose the beam of a 5 mW helium-neon laser was expanded to cover the complete active area of the PMT, and attenuated by a factor $10^3$ with two neutral density filters (ND2 and ND3). This yielded an intensity comparable to that measured in the light scattering experiments, which enabled determination of the PMT current as a function of the applied voltage. The photomultiplier conversion curves, shown in Appendix 3B, can be characterized with a simple linear relation of the form

$$\log\left(\frac{I}{P}\right) = C_1 + C_2 \log(\Delta V)$$  \hspace{1cm} (3.20)

in which $I$ is the PMT current, $P$ the total power of the radiation striking the PMTs surface, $\Delta V$ the applied voltage and $C_1$ and $C_2$ are constants. The following values were found for the calibration constants:

- 90° PMT (Nr. 5083): $C_1 = -21.13$ and $C_2 = 8.503$
- 43° PMT (Nr. 5084): $C_1 = -20.49$ and $C_2 = 8.181$

The output current from the photomultiplier is fed to a transimpedance amplifier which is used at the 1 mV/μA setting. Before being stored by the digital oscilloscope the signals are amplified by a factor of approximately 33. An empirical loss factor is included in the model, to account for reflections by the lens and window surfaces, the transmission characteristics of the long wave pass filters and the partial obscuration of the scattering volume by the electrode grid.

If the time-dependent scattering signal is to be modelled, particle motion has to be considered as well. The situation is relatively simple, because the measuring volume is located far enough from the nozzle exit for all particles to reach their terminal velocity. The fitting results from the centreline approximation described in Appendix 2C will be used here:

$$\log(v) = 2.358 - 0.4361 \times \log(d_p) - 0.08677 \times \log^3(d_p)$$ \hspace{1cm} (2C.7)
Figure 3.8 Response curves for the 90° (top) and 43° detectors (bottom), calculated with MIECONEi. The calculations were performed for polystyrene latex (N=1.587+0i) and corn oil (N=1.473+0i).
3.4.2 Modelling results

With the models described in the previous section and Appendix 2A the time and trajectory dependent signal from a particle of arbitrary size can be predicted. Figure 3.9 shows two signals for a 1 µm particle, passing through the centre and the edge of the laser focus.

![Graph showing voltage vs time for a 1 µm particle](image)

Figure 3.9 Model predictions of the scattering signal for a 1 µm particle passing through the centre (solid line) and edge (dotted line) of the laser focus.

Unfortunately, the model predictions are not accurate enough to allow for quantitative comparison with the experimental results. However, the model can be used to gain insight into the general behaviour of the system. With this goal in mind it was decided to model a collection of monodisperse particles, randomly seeded in the aerosol beam. Three characteristic parameters were calculated for every particle: the maximum voltage, the signal area, and the peak width. The width of a distribution can be characterized by several parameters, including full width at half maximum (FWHM), standard deviation (σ) and interquartile range (Q). The experiments had shown that the interquartile range of the scattering peaks gave the lowest spread for a monodisperse aerosol, and it was therefore adopted as the parameter for characterizing peak width. The interquartile range is defined as the time difference between the points where the cumulative voltage distribution exceeds 25% and 75% of the total peak area. The concept of the interquartile range for this particular case is illustrated by Figure 3.10, drawn on the next page.
Figure 3.10 The interquartile range is determined from the points where the cumulative signal exceeds 25% and 75% of the peak area.

The modelling results show that the maximum voltage and signal area behave in a very similar way. There are small differences for particles passing through the laser beam at different positions, but since this effect is caused by the difference in beam width it will not be considered here. Figure 3.11 shows a histogram of the distribution of peak area values calculated from a Monte Carlo simulation of 1000 particles ($d_p=4\ \mu m$).

Figure 3.11 Peak area distribution for a population of 1000 4\ \mu m\ particles (simulations).
The particles were seeded uniformly in an aerosol beam with a radius of 40 μm, crossing the laser beam at its waist. The particle velocity was taken from Equation 2C.7, and the laser intensity from Equation 3.18. The time dependent signal was calculated for particles with radial distances not exceeding (w(z)/w(0))×15 μm. The column width of the histogram was calculated with a kernel estimator

\[
h = \frac{0.9 \times \text{min}(\sigma, Q/1.34)}{n^{0.2}} \tag{3.21}
\]

In this equation \( h \) represents the bandwidth of the kernel, which was adopted as the column width. ‘\( \text{min} \)’ indicates that either the standard deviation \( \sigma \), or the interquartile range \( Q \) divided by 1.34 has to be inserted, whichever has the lowest value. \( n \) is the total number of observations. The figure shows how the results are influenced by the intensity ambiguity problem described in Section 3.2.3. The majority of particles produce a low peak area, since they pass through the edges of the laser beam. The somewhat flat centre of the radial intensity profile (see also Figure 3.3) causes a second maximum in the distribution curve at high area values. The modelling results demonstrate that the peak area itself cannot be used to characterize the size of a single particle.

The peak width for a monodisperse particle population, characterized by its interquartile range, shows a significant spread. However, as it is not so clear how the distribution is produced, the relation between the peak width and the position of the particle trajectory was investigated. Because of the intensity distribution function (Equation 3.18) it was expected that peak width would increase with the axial position, as was confirmed by the modelling results. The radial position also has a notable effect on the width of the scattering peaks, as is illustrated by Figure 3.12.

Figure 3.12 Surface plot of the peak width calculated as a function of the axial and radial position.
It was found that the peak width in the laser focal plane \((x=0)\) has its maximum value when the particle passes through the centre of the laser beam \((z=0)\). This effect is caused by the radial intensity profile and it is much more pronounced for multi-mode lasers. If the same calculations are repeated for a Gaussian beam profile, no variation in peak width is observed. The experimental results (section 3.4.4) will show that the described effect also occurs in reality.

### 3.4.3 Data reduction

As described in section 3.3.2, two detectors are used to avoid false triggers from dark spikes and to gather extra information. Every scattering event yields two waveforms of two microseconds length, recorded at a sampling frequency of 500 megasamples per second (see Figure 3.13).

![Graph](image)

**Figure 3.13** Typical example of a signal pair recorded for a 4 μm oil particle.

This implies that every particle produces a data array of 2000 numbers and it is obvious that some kind of data reduction is required. Five parameters were determined for every signal stored:

1. **Background level** \((V_{bg})\). Because the sample time of 2 μs exceeds the duration of the light scattering pulse, part of the signal represents the situation where no particle is present in the laser beam. By calculating the average value of the voltage for this part an estimate of the current background level is obtained.

2. **Amplitude.** The amplitude of the scattering signal is defined as the maximum voltage in a waveform minus the background level.
Centre. The position of the scattering peak within the data array is characterized by \( t_{\text{centre}} \) which is essentially the first moment about the origin of the voltage distribution after background subtraction:

\[
 t_{\text{centre}} = \frac{\sum_{i=0}^{n} t_i (V(t_i) - V_{bg})}{\sum_{i=0}^{n} (V(t_i) - V_{bg})}
\]  

(3.22)

Area. The scattering signal is integrated over an interval of half width 500 ns, symmetrically around the peak centre. The area is corrected for the background level.

Width. The width of the scattering peak is characterized by the interquartile range, as described in the previous section.

After calculating all five parameters for the recorded signals the internal consistency was tested. The following properties were considered:

- Simultaneity. For every signal pair (the 45° and 90° data) the difference between the two peak centres (\( \Delta t_{\text{centre}} \)) can be calculated. Because both signals originate from one scattering event their centres should be located at the same point in time.
- Similarity (a). The two peaks in a signal pair should have the same width, since the width is only determined by the particle trajectory.
- Similarity (b). Since the signals are produced by monodisperse particles, the ratio of the two signal levels (the signal area ratio for example) should have a constant value.

For the three properties listed above the appropriate parameters are calculated: the difference between the peak centres, the logarithm of the ratio of peak widths and the logarithm of the ratio of peak areas. The reason why the logarithm of a ratio is used instead of the ratio itself is that a log-normal distribution is expected. Subsequently distributions are constructed and the quartiles \( Q_{.25} \) and \( Q_{.75} \) and the interquartile ranges \( Q \) are determined. Signals are accepted when each of the three examined quantities lies within the interval \([Q_{.25} - 1.5Q; Q_{.75} + 1.5Q]\). The standard deviation for the difference in peak centre typically ranges from 40 to 120 ns, and the standard deviation for the width ratio is usually in the range from 0.25 to 0.5. The spread in area ratio was found to vary for the examined data sets. After reduction the datasets contained 75 to 97 % of the original number of observations.

From ten data sets, each representing one population of monodisperse particles, the distributions of amplitudes, peak centres, areas and widths are constructed. The 0.501 μm polystyrene latex and 4 μm corn oil data were chosen as typical examples of small and large particles, and Appendix 3C shows the relevant distributions as plots of the kernel estimator. The kernel estimator is an alternative for the familiar histogram, which uses the kernel function \( K \) with bandwidth \( h \), given by Equation 3.21.
the following definition is given by Silverman (1986):

$$f_{nh}(x) = \frac{1}{nh} \sum_{i=1}^{n} K\left( \frac{x - X_i}{h} \right)$$  \hspace{1cm} (3.23)

and a frequently used kernel function is the Epanechnikov kernel:

$$K(x) = \begin{cases} 
\frac{3}{4}(1 - x^2), & \text{for } x \in [-1,1] \\
0, & \text{for all other } x
\end{cases}$$  \hspace{1cm} (3.24)

3.4.4 Experimental results: detection efficiency

The experiments indicate that the number of signals measured per unit time varies with particle size. This was to be expected, since a large particle can already produce a measurable scattering signal for an intensity where small particles remain undetected. Looking at the contours in Figure 3.7, it is clear that the measurement volume increases with particle size, as does the number of particles which passes through the volume per unit time. Unfortunately, a malfunctioning optical particle sizer (Climet Ci-226M + Ci-1000 combination) permitted the measurement of number concentrations for particles of 2 μm and larger only, which limited the possibilities. Table 3.3 summarizes the results, with the transmitted rate calculated according to the modelling results (see also section 2.4.6). The last column contains the detection efficiency, i.e. the fraction of particles really detected, based on the number of particles transmitted to the analysis section.

Table 3.3 Rate at which corn oil particles are detected, compared to the rates at which they enter the aerosol beam generator and the measurement volume. The 16 mW helium-neon detection laser was focused to a spot size of approximately 20 μm.

<table>
<thead>
<tr>
<th>particle size (μm)</th>
<th>ingoing rate (s⁻¹)</th>
<th>transmitted rate (s⁻¹)</th>
<th>detected rate (s⁻¹)</th>
<th>detection efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>118</td>
<td>77</td>
<td>1.3</td>
<td>0.017</td>
</tr>
<tr>
<td>4</td>
<td>296</td>
<td>296</td>
<td>15</td>
<td>0.050</td>
</tr>
<tr>
<td>6</td>
<td>123</td>
<td>123</td>
<td>19</td>
<td>0.154</td>
</tr>
<tr>
<td>8</td>
<td>169</td>
<td>169</td>
<td>67</td>
<td>0.396</td>
</tr>
</tbody>
</table>

The results clearly show that the fraction of particles detected by the light scattering setup is a strong function of particle size (size biasing). If a particle size distribution is to be constructed from the data, it is necessary to correct for this effect by dividing the number of particles in a size class through the relevant detection efficiency.
3.4.5 Experimental results: area ratio

The modelling results predict a wide spread in peak area, even for a monodisperse aerosol. This prediction is confirmed by the experiments, as can be seen from studying the figures 5, 6, 13 and 14 in Appendix 3C. An alternative approach is to calculate the ratio of the signals from the detectors at 45° and 90°. Since both signals originate from the same scattering event their ratio should be constant, provided the response functions of the PMT and electronics do not change in time. Figure 3.14 shows the area distribution for the 4 μm corn oil aerosol, plotted as the logarithm of the ratio. The distribution can be characterized by the average ratio (3.52) and its geometric standard deviation (0.58), which is approximately 17%. The relative standard deviation of the signal area itself (measured at 45°) is about 50%, which indicates that the area ratio is a more consistent parameter for a monodisperse aerosol. This result suggests that the area ratio is indeed independent of particle trajectory.

![Graph showing area ratio distribution for the 4 μm corn oil aerosol.](image)

Figure 3.14 Area ratio distribution for the 4 μm corn oil aerosol.

The average area ratio has been calculated for each of the ten data sets and the results are plotted on the next page, as a function of particle size (Figure 3.15). The plot also contains the theoretical curve for corn oil, calculated from Mie theory. It is obvious that the oscillatory behaviour of the calculated curve makes it impossible to compare experimental and theoretical values.
At this point it should be remembered that by adopting Mie theory it was implicitly assumed that the incident radiation can be considered a plane wave. In practice, the wave front is somewhat curved because of the focusing optics. This effect can be incorporated in the calculations by averaging the signal over a small interval around the scattering angle. A simple averaging algorithm which serves our purpose is for example given by $x_{i,\text{new}} = \frac{1}{3}(x_{i-1,\text{old}} + x_{i,\text{old}} + x_{i+1,\text{old}})$. It was found that the strongest fluctuations have disappeared from the area ratio function when the averaging algorithm has been applied one hundred times. A plot of the area ratio calculated in this way against the experimental values (Figure 3.16, next page) supports the hypothesis that a linear relationship exists between the two. In theory all points should satisfy the relation $y = x$, and the experimental slope of 0.748 indicates a difference in response between the two detection systems. The difference can for instance be caused by partial obscuration of the detection optics by the ion optics, or by errors in the functions used in the theoretical calculations. Because of the oscillations in the area ratio function, large deviations from the linear relationship can be expected. The curve shows a sharp increase for particle diameters between 0.1 and 0.5 μm, and a small difference in diameter can therefore result in a large difference in area ratio and thus in a deviation from the linear relation found in Figure 3.16. The deviation found for the 2 μm corn oil data point cannot be explained in this way.
Figure 3.16 Experimental area ratios plotted against the theoretical values obtained from the smoothed response curves. The errorbars indicate one standard deviation.

In conclusion it can be stated that although the area ratio is constant for monodisperse particles, it is not easy to use as a measure for particle size. It is not clear to what extent the oscillations in the response curve are suppressed in practice, but a unique relationship will not be found. It can therefore be concluded that the area ratio does not give a unique measure for the particle size in the present configuration.

3.4.6 Experimental results: peak width

The simulation described in sections 3.4.1 and 3.4.2 predicts a wide spread in peak width and the experimental results confirm this prediction. As a result, peak width is not a very good parameter for characterizing the size of single particles. It is however possible to obtain a rough estimate of the (average) particle size of a monodisperse aerosol, as will be illustrated using Figure 3.17a. In this figure the peak width of the individual measurements for the 4 μm particles is plotted as a function of signal amplitude. It should be noted that the plot is qualitatively very similar to the simulation results, shown in Figure 3.17b.
Figure 3.17 Graphs of the peak width as a function of the signal amplitude. Shown are the experimental results for the 4 µm corn oil aerosol (a) and the model calculations for the same particle size (b).
For smaller particles the data points shift to the left-hand side, and at a certain amplitude value they will fall beneath the detection limit and disappear. In order to overcome this problem the peak width at maximum amplitude is chosen as characteristic parameter for a particle population. This value represents the response for particles passing through the centre of the laser beam, which is the most consistent parameter when data sets for different particle sizes are to be considered. It can however be difficult to obtain this parameter from a limited number of observations. It was therefore decided to determine the mean value of the peak widths of all data points that lie within a rectangle 10% of the maximum amplitude wide and 50 ns high. Table 3.4 summarizes the results for the ten data sets.

Table 3.4 Peak widths at maximum amplitude for the PSL and corn oil aerosols examined in the present study.

<table>
<thead>
<tr>
<th>particle size (µm)</th>
<th>peak width at 45° (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.364</td>
<td>129</td>
</tr>
<tr>
<td>0.501</td>
<td>133</td>
</tr>
<tr>
<td>1</td>
<td>127</td>
</tr>
<tr>
<td>1</td>
<td>126</td>
</tr>
<tr>
<td>1.01</td>
<td>111</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
</tr>
<tr>
<td>2.26</td>
<td>136</td>
</tr>
<tr>
<td>3.09</td>
<td>182</td>
</tr>
<tr>
<td>4</td>
<td>203</td>
</tr>
<tr>
<td>6</td>
<td>199</td>
</tr>
</tbody>
</table>

To allow for comparison of these results with the model described in Appendix 2C the reciprocal value of the peak widths is calculated, being a measure for the particle velocity. The results are plotted on the next page in Figure 3.18, together with the terminal velocities obtained from the model calculations. It should be noted that the quantities have different dimensions, and therefore no conclusions can be drawn from the offset between the two. The figure shows that the experimental results and the theoretical curve display the same trend and that the difference in mass density between polystyrene latex and corn oil (1050 and 920 kg/m³ respectively) has little influence. These observations support the hypothesis that the peak width is in fact linked to the particle terminal velocity. If the spread in peak widths for a population of monodisperse particles could be reduced it should be possible to use the peak width for characterizing the size of individual particles.
3.5 Conclusions and discussion

The experiments have shown that particles as small as 0.364 μm can be detected satisfactorily with the present setup. In contrast, it can be concluded that an unambiguous determination of the size of single particles is not possible. The area ratio method, described in section 3.4.5, yields a parameter which is characteristic for individual particles, but due to the oscillations in the light scattering response curve this parameter is not readily interpretable in terms of particle size. In contrast, the width of a scattered light peak is a direct measure for the (aerodynamic) size of a particle, but it is unfortunately also dependent on the particle trajectory. This makes the peak width unsuitable for determining the size of individual particles.

It is likely that some simple improvements will make the measurement of the size of individual particles feasible. The source of all problems is basically the variation in intensity found across the optical volume. If this variation is eliminated or significantly reduced, both the peak height and width would be usable parameters for characterizing particle size. A more uniform illumination intensity can be realized in a number of ways:

- By using only the centre part of the laser beam the intensity drop at the edge of the optical volume can be made much sharper. This can be achieved by limiting the collection angle of the detection
optics, or by expansion of the laser beam followed by selective transmission of the beam centre. A disadvantage of this solution is that either the size of the optical volume or the intensity has to be reduced, which will consequently reduce the performance of the instrument.

- A similar approach changes the aerosol beam instead of the laser beam; restricting the aerosol beam to the centre of the laser focus ensures a more uniform illumination intensity. This can be achieved by reducing the diameter of the second skimmer or using sheath air (see also section 2.4.5), but this decreases the rate at which particles are transferred to the analysis section. An alternative solution would be to apply aerodynamic lenses (Liu et al. 1993), which move the particles closer to the centreline of the beam. Unfortunately the latter method is not suitable for particles of 1 μm and larger.

- There are optical systems available which change the radial intensity profile of a laser beam through the application of anamorphic prisms and other components (Thomson et al. 1994). With these so-called beam shaping optics it is possible to create a top-hat profile, which ensures uniform illumination of the optical volume.

A fundamentally different method of particle size measurement uses the time which elapses when a particle traverses a known, fixed distance. With this method, originally developed by Dahneke and coworkers (1972), the particle time-of-flight is usually obtained from the scattered light pulses from two laser beams. In our setup the concept is probably easiest implemented by splitting the laser beam already in use, or by adding a second one. This method functions practically independent of the optical properties of the particles, but results are influenced by particle shape and density and by the gas pressure and temperature. A second technique using two laser beams is the phase-Doppler method, which is also an interesting alternative. Besides being independent of the incident light intensity, it can optionally measure a light scattering diameter or - from the velocity - an aerodynamic diameter.

References

Burle (1980).


Accurate determination of fiber radii in the hypermicrometer range by multiwavelength laser light scattering, Appl. Opt. 18, 3751-3757.

The phase-Doppler method applied to very small particles, Part. Part. Syst. Charact. 11, 55-62.
Appendix 3A Calculation of beam and focus diameters using the ABCD law

The following section describes how beam diameters can be calculated, and it was largely derived from Guenther (1990). It is convenient to define a coordinate system with cylindrical symmetry, as depicted on the right. Light rays can be represented as a vector field with a radial ordinate $x$ and angle $\gamma$. It is assumed that $\gamma$ is small (paraxial approximation), which allows the sine and tangent functions to be replaced by their angle in radians. The influence of an optical system on a light ray can be deduced from the so-called ABCD matrix, which relates the input parameters (denoted by the subscript 1) to the output parameters (subscript 2):

$$
\begin{pmatrix}
  x_2 \\
  \gamma_2 
\end{pmatrix}
= 
\begin{pmatrix}
  A & B \\
  C & D 
\end{pmatrix}
\begin{pmatrix}
  x_1 \\
  \gamma_1 
\end{pmatrix}
$$

(3A.1)

It can be shown (Guenther 1990) that the transfer matrix for a Gaussian wave propagating through space over a distance $d$ is:

$$
\begin{pmatrix}
  1 & d \\
  0 & 1 
\end{pmatrix}
$$

(3A.2)

For a thin lens with focal distance $f$ the transfer matrix becomes:

$$
\begin{pmatrix}
  1 & 0 \\
  -\frac{1}{f} & 1 
\end{pmatrix}
$$

(3A.3)

Please note that substituting $d=f$ in the transfer matrix for a thin lens yields $x=0$, which indicates that the ABCD matrix method cannot be used directly for the calculation of beam dimensions. The paraxial approximation will therefore be applied to the Helmholtz equation.

Through this approach solutions are obtained, which display Gaussian amplitude distributions. These distributions can be characterized by the complex size parameter $q$, which is related to the radius of curvature of the phasefront of the wave ($R$), as measured from the position of minimum beam waist.
\[ \frac{1}{q} = \frac{1}{R} \frac{i\lambda}{\pi w^2} \]  

(3A.4)

A well-known equation for a Gaussian spatial amplitude distribution is given by:

\[ E = E_0 \exp \left[ -\frac{x^2 + y^2}{w^2} \right] \]  

(3A.5)

The beam waist \( w \) equals the half-width of the Gaussian function at the point where the amplitude is \( 1/e \) of its maximum value \( (E_0) \). The minimum beam waist \( w_0 \) can be related to the confocal parameter \( q_0 \)

\[ q_0 = \frac{\pi w_0^2}{\lambda} \]  

(3A.6)

The parameter \( q_0 \) can be interpreted as the minimal value of the complex size parameter \( q_0 \)

\[ q_0 = i q_0 = \frac{i\pi w_0^2}{\lambda} \]  

(3A.7)

In practice, the only parameters known are the beam waist \( w_z \) at the laser exit window \((z=z_1)\), and the divergence half angle \( \theta \). For small values of \( \theta \) a rough estimate of the minimal value of the beam waist can be found from

\[ \theta = \frac{\lambda}{\pi w_0} \]  

(3A.8)

and \( z_1 \) can be found from

\[ w_z^2 = w_0^2 + \theta z_1^2 \]  

(3A.9)

To enable calculation of the beam waist \( w_z \) at an arbitrary point along the optical axis, the complex size parameter must be known at a reference plane, for example where \( z=z_1 \). With Equations 3A.8 and 3A.9 the radius of curvature at \( z_1 \) \((R_z)\) can be calculated

\[ R_z = \frac{z_1}{1 + \left( \frac{\pi w_0^2}{\lambda z_1} \right)} \]  

(3A.10)

By substitution of \( R_z \) and \( w_z \) into Equation 3A.4 \( q_z \) can be obtained.
Next step is to apply the ABCD law to the complex size parameter \( q_1 \) in order to obtain the parameter \( q_2 \) at an arbitrary point on the optical axis. In the paraxial approximation the following relationship holds

\[
\gamma = \frac{dx}{dz} = \frac{x}{R},
\]

\( (3A.11) \)

Substitution into Equation 3A.1 yields

\[
R_z = \frac{x_z}{\gamma_z} = \frac{AR_1 + B}{CR_1 + D},
\]

\( (3A.12) \)

and because of the formal equivalence between \( q \) and \( R \) (Equation 3A.4)

\[
q_2 = \frac{x_z}{\gamma_z} = \frac{Ar_1 + B}{Cr_1 + D}
\]

\( (3A.13) \)

The beam waist can be found by analysing the complex part of \( 1/q_2 \):

\[
w_2 = \text{Re} \left( \frac{\lambda}{\pi} \right) \left( -\text{Im} \left( \frac{1}{q_2} \right) \right)
\]

\( (3A.14) \)

Writing out the ABCD matrix for the complete optical system makes it possible to calculate the beam waist at any point. This has been done for a system consisting of two lenses, placed at 6 cm \((f=6 \text{ cm})\) and at 29.5 cm \((f=5 \text{ cm})\) from the laser exit window. The helium-neon laser used has a specified beam width of 1.47 mm and a full divergence angle of 1.4 mrad. With these data Equation 3A.14 can be simplified to yield the beam waist \( w_2 \) as a function of \( z \):

\[
w_2 = \sqrt{6.0665 \times 10^{-4} z^2 + 6.6879 \times 10^{-11}}
\]

\( (3A.15) \)

This relation holds for \( z \geq 7.067 \text{ cm} \), i.e. beyond the second lens. At the focal point, located at \( z=0 \), the beam waist is 8.2 \( \mu \text{m} \), and thus the focal size is estimated to be 16.4 \( \mu \text{m} \).
Appendix 3B Calibration curves for the photomultipliers 5083 and 5084.

Figure 3B.1 Calibration curve for the photomultiplier Thorn EMI model 9202B, nr. 5083.
Figure 3B.2 Calibration curve for the photomultiplier Thorn EMI model 9202B, nr. 5084.
Appendix 3C Kernel estimators of the experimental light scattering data for 0.501 μm PSL and 4 μm corn oil particles

Figure 3C.1 Amplitude distribution for the 0.501 μm PSL aerosol measured with the 45° detector.

Figure 3C.2 Amplitude distribution for the 0.501 μm PSL aerosol measured with the 90° detector.
Figure 3C.3 Peak centre distribution for the 0.501 μm PSL aerosol measured with the 45° detector.

Figure 3C.4 Peak centre distribution for the 0.501 μm PSL aerosol measured with the 90° detector.
Figure 3C.5 Peak area distribution for the 0.501 μm PSL aerosol measured with the 45° detector.

Figure 3C.6 Peak area distribution for the 0.501 μm PSL aerosol measured with the 90° detector.
Figure 3C.7 Peak width distribution for the 0.501 μm PSL aerosol measured with the 45° detector.

Figure 3C.8 Peak width distribution for the 0.501 μm PSL aerosol measured with the 90° detector.
Figure 3C.9 Amplitude distribution for the 4 μm corn oil aerosol measured with the 45° detector.

Figure 3C.10 Amplitude distribution for the 4 μm corn oil aerosol measured with the 90° detector.
Figure 3C.11 Peak centre distribution for the 4 μm corn oil aerosol measured with the 45° detector.

Figure 3C.12 Peak centre distribution for the 4 μm corn oil aerosol measured with the 90° detector.
Figure 3C.13 Peak area distribution for the 4 µm corn oil aerosol measured with the 45° detector.

Figure 3C.14 Peak area distribution for the 4 µm corn oil aerosol measured with the 90° detector.
Figure 3C.15 Peak width distribution for the 4 μm corn oil aerosol measured with the 45° detector.

Figure 3C.16 Peak width distribution for the 4 μm corn oil aerosol measured with the 90° detector.
Laser-ionization of aerosol particles

4.1 Introduction

If an on-line mass spectrometric analysis of a single aerosol particle is to be performed, it is necessary to generate a measurable amount of ions from that particle. This is not a trivial problem, because the particle is very small and it moves with a high velocity (50 to 500 m/s). Laser-ionization has a much higher energy transfer rate than conventional techniques such as electron ionization (Steenvoorden 1993). It generates a short burst of ions, from which a complete mass spectrum can be obtained by using a time-of-flight analyzer. It has the additional advantage that the amount of energy deposited in a sample is easy to adjust, enabling the measurement of either elementary composition or molecular structure. Laser-ionization is generally applicable and not limited to thermally unstable compounds, as is the case with thermal ionization (Vertes et al. 1993). Finally, the technique can induce fragmentation and ionization in one single step. It was therefore decided to use laser-induced fragmentation in this project.

This chapter will be devoted to the interaction of radiation with matter, with emphasis on the ion formation from aerosol particles in vacuum. The modelling of the interaction of radiation with an aerosol particle is the subject of section 4.2, and models for the moderate irradiance and high irradiance regimes are presented in sections 4.2.2 and 4.2.3. Section 4.3 discusses the experiments performed in the present study. It concludes with a discussion of the experimental results in relation with the model predictions and literature values.

4.2 The interaction of radiation with an aerosol particle

4.2.1 General description of the interaction physics

This section gives a survey of the interactions between an aerosol particle and an incident laser beam. The intensity of the laser beam, often called irradiance, is one of the key parameters. Three irradiance regimes can be distinguished: low irradiance, where linear scattering and absorption processes dominate, moderate irradiance which induces droplet heating and vaporization, and high irradiance, characterized by hydrodynamic, plasma and nonlinear effects. Next to irradiance other parameters are important, such as the wavelength of the radiation, the size, shape and
optical properties of the particle, and conclusively the nature of the transport medium (solid/liquid, gas or vacuum). The remainder of this section is a brief description of the physics of the three fore-mentioned interaction regimes. For more information on this subject the reader is referred to extensive reviews published by Ready (1971), Armstrong (1988) and Lushnikov and Negin (1993), from which this section was partly derived.

For the low irradiance case (up to \(\sim 10^9\) W/m\(^2\)) interactions are described satisfactorily by the Maxwell equations. The change in temperature due to the absorption of radiation is negligible and optical parameters like the index of refraction are still considered to be constant. In some cases (Burtscher et al. 1980) ultraviolet light can cause the emission of electrons from the material, a process generally known as photoelectric charging. The refractive index changes with the laser wavelength for all materials, but a general relation between the two does not exist. The wavelength is also included in the size parameter \(\alpha (=\pi d/\lambda)\), which decreases with increasing wavelength. Mie theory enables the calculation of the electric and magnetic fields both inside and outside a spherical particle. It shows that the electric effects always dominate over the magnetic effects, which can therefore be left out of consideration. An interesting aspect of the internal electric field is the occurrence of absorption centres ('hot spots'), especially for absorbing materials. This phenomenon, discussed in Appendix 4A, causes nonuniform heating for particles of increasing size parameter. Nonlinear processes start to play a role when the irradiance is higher and phase changes take place inside the particle.

At moderate irradiance (10\(^9\)-10\(^{11}\) W/m\(^2\)) a significant amount of energy is absorbed by the particle material, resulting in a rise of temperature. Changes in temperature are generally accompanied by phase changes (melting, boiling and evaporation), which can also change the shape of the particle. Additionally, short wavelengths may cause ionization and photodecomposition of the particle material. Park and Armstrong (1989) distinguish between fast and slow heating regimes, dependent on the time scale at which heating and internal thermal conduction take place. In the case of slow heating a quasi-steady-state approximation can be adopted, assuming that the particle surface remains in thermal equilibrium. This is the case when the rate at which energy is supplied by the laser beam equals the rate at which energy is removed by the vaporization process. This assumption is no longer valid for the fast heating regime, where nonequilibrium surface vaporization has to be taken into account. The vapour produced at this irradiance regime is usually transparent. A few years earlier Armstrong (1984) developed a similar model, based on the establishment of a steady-state, developed vaporization regime (DVR). The author claims that the model covers irradiances from 10\(^8\) to 10\(^{15}\) W/m\(^2\), but the DVR can best be compared with the slow heating regime mentioned earlier. It is therefore not likely to be valid for irradiances exceeding 10\(^{11}\) W/m\(^2\). The steady-state vaporization on which the DVR model is based will never be reached in the fast heating regime. Although a more realistic description of the absorption cross section is included in the fast/slow
heating model, the DVR model is to be preferred because of its simplicity. In contrast with the fast/slow heating model it does not require extensive numerical calculations and the identification of characteristic time scales increases physical insight. The DVR model does not cover the fast heating case, but it predicts threshold irradiances for nonequilibrium vaporization (i.e. fast heating) and plasma formation. It should be noted that both models were developed for particles suspended in air. It is not exactly clear how the absence of the suspending medium influences interactions for particles in vacuum, but it is assumed that the DVR model remains valid up to the point where convective terms start to play a role. The DVR model will be explained in section 4.2.2.

At high irradiance (above 10^{11} W/m^2) hydrodynamic effects start to play a role and particle and medium no longer remain at constant pressure. In vacuum these effects can only take place inside the particle, where they are usually manifested as shock waves. Liquid and/or vapour material can be expelled from the particle as a result (ablation). Furthermore the vapour species released from the surface interact with the incident laser pulse and become excited and ionized. Ions can be produced by thermal ionization, and by single- and multi-photon absorption processes including inverse Bremsstrahlung. With inverse Bremsstrahlung the kinetic energy of a free electron increases through photon absorption. This process is more efficient for long wavelengths, but for short wavelengths part of the absorption can be by photo-ionization, a process which produces free electrons and thus eases plasma ignition. The plasma formed in this way absorbs more and more radiation, until the electron density becomes sufficiently high so that the core of the plasma becomes opaque. Rayleigh scattering by ultrathin particles formed in the plasma plume decreases the penetration of the laser beam even further (Matsunawa 1990). As a consequence the particle becomes shielded from the incident laser beam, but the heat and radiation emitted by the plasma (Bremsstrahlung) are in general sufficient to sustain the vaporization and ionization processes. The plasma will continue to exist long after the laser pulse has ended. The expansion velocity is typically in the order of 10^4-10^5 m/s, which is two orders of magnitude higher than the velocity in the case of thermal evaporation at moderate irradiance. As a result, the remainder of the particle is propelled away from the plasma at a velocity of 10-100 m/s (Zhang et al. 1987). Plasma formation will be the subject of section 4.2.3.

4.2.2 Moderate irradiance: the DVR-model

Armstrong (1984) developed a relatively simple model to investigate the heating and vaporization processes for an irradiated aerosol particle: the 'developed vaporization regime' (DVR) model. This section discusses the model and additionally the concept of absorption centres. The model is claimed to be valid for irradiances ranging from 10^8 to 10^{15} W/m^2, but an upper limit of 10^{13} W/m^2 seems more realistic. It neglects hydrodynamic effects, which become increasingly important with increasing irradiance. A one-dimensional model by Vertes and coworkers (1989a), developed for
higher irradiance, does take these effects into account. Although this model uses the questionable concept of local thermal equilibrium (Schueler et al. 1983), it can be valuable for predicting the onset of plasma formation (see section 4.2.3).

With the DVR model, it is assumed that a steady-state distribution of electromagnetic energy is established in times in the order of the photon transit time ($10^{-13}$ s). The material absorbs part of the energy through inverse Bremsstrahlung, typically in $10^{-11}$ s. It is therefore safe to assume that the absorbed radiation is instantaneously converted into thermal energy. In the DVR model Armstrong adopts an approximation for the absorption cross section, originally suggested by Zeldovich and Raizer (1966). Particles are considered to be optically 'thick' or 'thin' according to whether the inequality $\kappa \sigma > 1$ or $\kappa \sigma < 1$ is satisfied, where $\kappa$ represents the bulk absorption coefficient and $\sigma$ the particle radius. A more detailed picture of the absorption cross section, often called the source function, can be obtained from Mie theory. Numerical results for several cases can be found in literature (Dusel et al. 1979, Greene et al. 1985, Chylek et al. 1987, Pinnick et al. 1990) and these are discussed in Appendix 4A. Variations in the source function are negligible for optically thin particles, and the distribution of beam energy is uniform within the particle. The situation is more complex in the case of optically thick particles. For small particles ($\alpha \ll 1$) the electric field is nearly uniform over the surface. In this case it is assumed that the energy distribution is uniform within a shell of thickness $\delta = \kappa^{-1}$ (the so-called $\delta$ zone) and zero elsewhere within the particle. The uniformity disappears for larger particles and absorption centres arise. The DVR model is not valid for this class of particles. In conclusion, $\delta = \sigma$ for optically thin particles, and $\delta = \kappa^{-1}$ for optically thick particles which are small compared to the wavelength ($\alpha \ll 1$).

It is assumed that variations in thermodynamic quantities propagate within the particle with the local speed of sound, $c_0$. The material in the $\delta$ zone increases its temperature, but remains locked in position for times smaller than the acoustic time $\tau_a$, defined by

$$\tau_a = \frac{\delta}{c_0} \quad (4.1)$$

This approximation no longer holds for sufficiently intense beams, and spontaneous evaporation takes place at a time $t \leq \tau_a$. This is the fast heating case, as defined by Park and Armstrong (1989). The minimum irradiance which will achieve this state can be estimated by

$$I_a = 4\rho c_0 L(T_v) \quad (4.2)$$

where $\rho$ is the mass density and $L(T_v)$ the heat of evaporation at an appropriate temperature $T_v$. Park and Armstrong call this temperature the superheat limit and found it to be related to the critical temperature by $T_v = 0.9 T_{cr}$. The heat of evaporation at temperature $T_v$ can be approximated by the relation.
\[ L(T_v) = L_0(T_m) + \frac{1.82RT_v}{m} - \frac{3RT_m}{m} \]  \hspace{1cm} (4.3)

In this equation \( L_0(T_m) \) is a literature value known at a reference temperature \( T_m \), \( R \) is the universal gas constant and \( m \) is the molar mass of the particle material. Park and Armstrong give an alternative relation for the threshold irradiance, which is a function of the thermal conductivity \( K \), the temperature variation \( \Delta T \) corresponding to the radial variation \( \Delta r \), the laser wavelength \( \lambda \), the normalized source function (absorption cross section) \( S \) and the complex index of refraction \( N \):

\[ I_{sf} = \frac{K\Delta T\lambda}{4\pi S(\Delta r)^2 \text{Re}(N)\text{Im}(N)} \]  \hspace{1cm} (4.4)

At even higher irradiance a plasma can form, and Armstrong gives the following relation for the threshold intensity \( I_\nu \) related to the ionization energy \( E_i \) per unit of mass

\[ I_\nu = 4\rho c_0 E_i \]  \hspace{1cm} (4.5)

Because plasma formation is the subject of section 4.2.3 it is not discussed here.

Material will evaporate from the \( \delta \) zone for times exceeding \( \tau_\nu \). In the case of optically thick particles, the characteristic time required for heat to diffuse out of the \( \delta \) zone with specific heat \( C \) and thermal conductivity \( K \) into the particle is given by

\[ \tau_\delta = \frac{\rho \delta^2}{4K} \]  \hspace{1cm} (4.6)

Steady-state vaporization of the \( \delta \) zone takes place for times \( t \leq \tau_\nu \) provided the energy delivered by the laser beam is sufficient to sustain this process. An energy balance over the \( \delta \) zone yields the threshold irradiance for DVR formation

\[ I_{DVR} = \frac{4\rho \delta L(T_{DVR})}{t} \]  \hspace{1cm} (4.7)

In this equation \( L(T_{DVR}) \) represents the heat of vaporization at the DVR temperature and \( t \) is time, which has a maximum value equal to the laser pulse length. In conclusion, the DVR occurs in the range \( \tau_\nu \leq t \leq \tau_\delta \) for the corresponding range of intensities

\[ I_\delta \leq I_{DVR} \leq I_\nu \] \hspace{1cm} with \( I_\delta \) given by

\[ I_\delta = 4\rho c_0 \frac{L}{\tau_\delta} \]  \hspace{1cm} (4.8)

Vaporization of the complete particle has to be taken into account in the case of optically thin particles, and for optically thick particles at times exceeding \( \tau_\delta \). Analogous to Equation 4.6, the characteristic time for heat to diffuse throughout the complete particle can be defined as
\[ \tau_0 = \frac{\rho C \sigma^2}{4K} \]  

(4.9)

In this case a DVR is established when \( \tau_0 \leq t \leq \tau_\delta \), and for the range of intensities

\[ I_{DVR} \leq I_\delta \]  

with \( I_{DVR} \) and \( I_\delta \) given by

\[ I_{DVR} = \frac{\rho L_0 V(t)}{\pi \sigma^2 t} \]  

(4.10)

\[ I_\delta = \frac{4\rho \sigma L_0}{3\tau_\delta} \]  

In these equations \( V(t) \) denotes the time dependent volume of the heated region and \( L_0 \) represents the heat of vaporization at a reference temperature. The two remaining regions described in Armstrong’s model (the numbers IV and V) do not apply in this particular case, because external conductivity effects are not relevant for a particle in vacuum.

The application of classical thermodynamics and the conservation laws for mass, momentum and energy yield differential equations for the change of temperature with time.

\[ \frac{\partial T}{\partial t} = \frac{I}{4\rho \delta C} \quad \text{when} \quad 0 \leq t \leq \tau_\delta \]  

(4.11)

\[ \frac{\partial T}{\partial t} = \frac{I}{4\rho \delta C} \left( 1 - 4L_0 m(t)/I \right) \quad \text{when} \quad \tau_\delta \leq t \leq \tau_\gamma \]  

(4.12)

\[ \frac{\partial T}{\partial t} = \frac{3\sigma^2 I}{4\rho C} \left[ 1 - 4L_0 m(t)/I \right] \quad \text{when} \quad \tau_\gamma \leq t \leq \tau_\sigma \]  

(4.13)

\[ \frac{\partial T}{\partial t} = \frac{3I}{4\rho \sigma C} (1 - 4L_0 m(t)/I) \quad \text{when} \quad \tau_\sigma \leq t \]  

(4.14)

In these equations \( \nu \) is the diffusion velocity at which the boundary of the heated region moves towards the centre of the particle.

\[ \nu = \sqrt{\frac{4K}{\rho C \delta t}} \]  

(4.15)

The mass flux \( m(t) \) is given by

\[ m(t) = \frac{\varepsilon P_s(T)}{\sqrt{2\pi RT/m}} \]  

(4.16)

in which \( \varepsilon \) is the evaporation coefficient and \( P_s(T) \) the saturation pressure at temperature \( T \). The evaporation coefficient gives the fraction of vapour molecules captured by the surface of the particle. Numerical integration
of the listed differential equations yields the time history of the particle temperature, as shown by Armstrong. It is however difficult to obtain information on how parameters like κ, ε and L depend on temperature and laser wavelength. As an example, Figure 4.1 (constructed using Armstrong’s results) shows how the temperature of a 1 μm water droplet changes with time. As this is an optically thin particle, the droplet temperature at a certain moment in time is assumed to be constant over the particle volume.

![Temperature-time curves for a 2 μm water droplet, calculated for intensities of $10^{12}$, $10^{13}$, $10^{14}$ and $10^{15}$ W/m² (reproduced using data from Armstrong (1984)).](image)

**4.2.3 High irradiance: ionization and plasma effects**

Although not accounted for in the DVR model, the vapour produced during the laser pulse can become partly ionized. This becomes important when the irradiance is higher than $10^{11}$ W/m². Hillenkamp et al. (1985) distinguish four ion formation processes:

1. Thermal evaporation of ions from the sample,
2. thermal evaporation of neutral molecules from the sample followed by ionization in the gas phase,
3. laser desorption,
4. ion formation in a laser generated plasma.

The first two processes are called thermal, because they can also be induced by classical, radiative and conductive heating sources. Thermal evaporation of ions is quite common for metals and inorganic salts like alkalihalides (Jöst et al. 1982) and it has been demonstrated for a limited
number of organic compounds too (for example quaternary ammonium salts). Whether neutral molecules can be evaporated from the condensed phase depends on their volatility and thermal stability. Posthumus and coworkers (1978) demonstrated the intact desorption of large molecules like oligosaccharides, coated on a metal surface. The term desorption is used in case the transition of a molecule or ion from the condensed into the gas phase takes place under non thermal equilibrium conditions (i.e. the fast heating regime). The process of evaporation and heating continues until the electron density of the partially ionized gas becomes high enough for the inverse Bremsstrahlung process to begin. Cascade ionization increases the temperature and hence the absorption cross section, and a plasma is formed. The plasma mode is characterized by a high density of ions and electrons. It is therefore not suited for organic mass spectrometry, because excessive fragmentation leads to atomic ions and all structural information is lost. On the other hand, this mode has distinct advantages for the analysis of inorganic species, because the ion yield becomes nearly uniform for all elements. At very high irradiances ablation can produce clusters of molecules directly from the particle surface, which could lead to large ions. These conditions are usually not found in mass spectrometry experiments.

From the above overview it will be clear that plasma formation has a strong influence on the ion population. Only limited fragmentation takes place for irradiances below the plasma formation threshold, resulting in a mass spectrum with relatively large ions. Recombination processes inside the plasma dominate the ion formation for higher irradiances. The plasma ignition process is complicated and not fully understood. A rough estimate of the plasma formation threshold can be obtained from Armstrong (1984):

\[ I_p = 4 \rho c_0 E_1 \]

(4.5)

However, it is unlikely that this equation will produce accurate results because parameters like laser frequency, particle size and temperature history are not accounted for, and they can both increase and decrease the threshold. A more basic approach includes the consideration of the absorption of radiation by the plasma through inverse Bremsstrahlung. This process has been investigated in plasma physics and several relations have been suggested for the absorption coefficient (see e.g. Ready 1971, Vertes et al. 1989 and Matsunawa 1990). Absorption increases rapidly with the electron density, until the frequency of plasma oscillation becomes comparable to or greater than the angular frequency of the laser. The plasma oscillation frequency \( \omega_p \) is given by

\[ \omega_p = \sqrt{\frac{n_e e^2}{\varepsilon_0 m_e}} \]

(4.17)

In this equation \( n_e \) is the electron number density, \( e \) the elementary charge, \( \varepsilon_0 \) the permeability of vacuum, and \( m_e \) the electron mass. The plasma becomes opaque with increasing absorption. For long wavelengths this is at lower free electron densities than for short wavelengths. However, for
short wavelengths the occurrence of photo-ionization produces free electrons which promote plasma formation.

For a realistic estimate of the plasma formation threshold both the condensed phase and the plasma absorption have to be considered. Vertes et al. (1989, 1989a) defined the plasma ignition threshold as the point where the importance of plasma absorption surpasses the importance of ordinary absorption. A time dependent model of energy deposition and plasma expansion is needed to estimate this threshold. The model assumes that the deposition of laser energy is an adiabatic absorption process. The approximation holds when light absorption and heating take place much faster than the expansion of the vaporized and ionized material. This implies that the adiabatic absorption of radiation and the expansion of the resulting plasma can be treated separately. In a one-dimensional model the energy balance is

$$\frac{\partial [\rho(E + v^2/2)]}{\partial t} = \frac{\partial}{\partial x} \left[ \rho v(E + p + v^2/2) - I \right]$$  \hspace{1cm} (4.18)

where \(v(x,t), p(x,t), \rho(x,t)\) and \(\rho(x,t)E(x,t)\) are the velocity, pressure, density and internal energy density of the material at a distance \(x\) from the surface, and \(I\) is the power density of the incident laser beam. From the assumption that expansion does not start during the laser pulse it follows that \(v=0\) during this phase and Equation 4.18 can be simplified to

$$\frac{\partial (\rho E)}{\partial t} = -\frac{\partial I}{\partial x}$$  \hspace{1cm} (4.19)

It should be noted that experimental evidence indicates that plasma formation often takes place at the beginning of the laser pulse, in which case the former simplification is not allowed. For the sake of simplicity this assumption will be applied anyway, even though it is questionable. The absorption of radiation can in general be described by

$$\frac{\partial I}{\partial x} = -\kappa I - \beta I^2 - \ldots$$  \hspace{1cm} (4.20)

where \(\kappa\) and \(\beta\) are the linear and first nonlinear absorption coefficients, respectively. For 'normal' light intensities nonlinear effects can be neglected, and only \(\kappa\), containing both surface \((\kappa_s)\) and plasma absorption \((\kappa_p)\), has to be considered. Although Vertes et al. (1989) never define 'normal', it is assumed that this condition applies to irradiances up to roughly \(10^{16}\) W/m².

$$\kappa = \kappa_s + \kappa_p$$  \hspace{1cm} (4.21)

As mentioned earlier, the plasma absorbs radiation mainly through inverse Bremsstrahlung. The absorption coefficient depends on the electron number density \((n_e)\), the electron temperature \((T_e)\) and the laser \((\omega)\) and plasma frequencies \((\omega_p)\):
\[
\kappa_{pl} = \frac{2\omega}{c} \text{Im} \left( 1 - \frac{\omega_{pl}^2}{\omega^2 \left( 1 + \frac{i}{\tau_{ei} \omega} \right)} \right)
\]

(4.22)

In this equation \( c \) is the speed of light and \( \tau_{ei} \) denotes the electron-ion collision time, which, in the case of singly charged ions, is given by

\[
\tau_{ei} = \frac{6\sqrt{2} \pi^{3/2} e^2 \alpha^2 m_e^{1/2} (k_B T_e)^{3/2}}{e^4 n_e \ln(\Lambda)}
\]

(4.23)

In this equation \( \ln(\Lambda) \) is the so-called Coulomb-logarithm, which corrects for Coulomb interactions in the electron-ion scattering process. It can be calculated from

\[
\Lambda = \frac{12\pi}{e^3} \sqrt{\frac{\varepsilon_0^3 k_B^3 T_e^3}{n_e}}
\]

(4.24)

In order to simplify calculations, Vertes assumes that the condensed phase absorption can be contributed to electronic and/or vibrational transitions in neutrals and ions, characterized by the molar absorption coefficients \( \varepsilon_N \) and \( \varepsilon_i \):

\[
\kappa_0 = \frac{n_{tot}}{N_A} (\varepsilon_N (1 - \eta) + \varepsilon_i \eta)
\]

(4.25)

In this equation \( n_{tot} = n_N + n_i \) is the number density in the solid containing both neutrals and ions. \( N_A \) represents Avogadro’s number and \( \eta \) is the degree of ionization. In this stage of the process the ions are likely to contribute little to the total absorption and their influence is in general negligible. It should be noted that molar absorption coefficients are usually expressed in cm\(^{-1}\)M\(^{-1}\) and that conversion to SI-units is required. The plasma ignition threshold is now defined as the point where absorption by the condensed phase and the plasma become equally important:

\[
\kappa_0(\eta) = \kappa_{pl}(n_e T_e)
\]

(4.26)

An expression for the internal energy of the target is needed in order to evaluate the plasma ignition threshold. In case the heat of melting and the heat of vaporization are negligible compared to the ionization energy \( E_i \), the internal energy of the target can be approximated by that of an ionized ideal gas:
\[ \rho E = n_{tot} \left[ \frac{3}{2} (1+\eta)k_B T + n\eta E_1 \right] \] (4.27)

Equation 4.19 can be integrated, assuming that during the laser pulse of length \( t \) the target reaches a final temperature \( T_2 \) and a degree of ionization \( \eta_2 \), which significantly exceed the initial values

\[ n_{tot} \left[ \frac{3}{2} (1+\eta_2)k_B T_2 + n\eta_2 E_1 \right] = (\kappa_0 + \kappa_p) t \] (4.28)

Combination of this equation with the condition for plasma ignition (Equation 4.26) enables the calculation of a threshold intensity, provided a relation between the temperature and the degree of ionization is available. If the local thermodynamic equilibrium hypothesis is adopted, the simplified Saha equation can be used:

\[ \frac{\eta^2}{1-\eta} = \frac{1}{n_{tot}} \left( \frac{2\pi k_B T e}{h^2} \right)^{3/2} \exp \left( -\frac{E_1}{k_B T_e} \right) \] (4.29)

where \( h \) represents Planck's constant. This yields the following expression for the plasma formation threshold:

\[ I_{thr} = \frac{3/2 (1+\eta_{thr})k_B T_{thr} + n_{thr} E_1}{2t} \frac{e}{N_A} (1-\eta_{thr}) \] (4.30)

The ionization potential can be used as a first approximation for the energy of ionization. However, a more appropriate value is obtained after correction for ion-ion interactions and influences from the external electric field. The first effect is expressed by the Debye-correction:

\[ \Delta E_D = \frac{e^2}{4\pi \varepsilon_0 \lambda_D} \] (4.31)

where \( \lambda_D \) represents the Debye length for a plasma containing only singly charged ions, given by

\[ \lambda_D = \sqrt{\frac{\varepsilon_0 k_B T_e}{2n_e e^2}} \] (4.32)

The Poole-Frenkel effect describes the lowering of the ionization energy due to the external electric field produced by the radiation \( E \), for a material with relative dielectric constant \( \varepsilon_r \).
\[ \Delta E_{pf} = \sqrt{\frac{e^3 E}{\pi \varepsilon_0 \varepsilon_r}} \]  

(4.33)

The average field strength of the electric field produced by radiation of intensity \( I_{thr} \) can be calculated from

\[ E = \sqrt{\frac{2 \varepsilon_0 I_{thr}}{c}} \]  

(4.34)

With these corrections the energy of ionization becomes

\[ E_i = E_p - \Delta E_D - \Delta E_{pf} \]  

(4.35)

4.3 Experimental section

4.3.1 The vaporization/ionization laser

The fragmentation and ionization of micrometre sized particles requires a laser with accurate control of the radiation, both spatially and temporally. Furthermore it was expected that a pulse energy in the order of one Joule would be needed to ensure complete fragmentation of large particles. A flash-lamps pumped Neodymium doped Yttrium Aluminium Garnet laser (Nd:YAG laser) was chosen for the given application (model HY1200 from Lumonics Ltd. Rugby U.K.). The fundamental wavelength of this laser type is 1064 nanometre, and other wavelengths are available through frequency doubling: the second and fourth harmonics, 532 and 266 nm respectively. The HY1200 is equipped with a passive Q-switch, in this case a dry KDP crystal. This material has non-linear characteristics, which cause a gradual build-up of energy in the laser medium. When the quality factor \( Q \), defined as the ratio of the stored energy over the dissipated energy is suddenly increased, a high power burst of light is produced. In this way Q-switching shortens the pulse length from 150 μs to 8 ns, creating a very high peak power (~10^8 W). With a well-designed lens system the laser beam can be focused to a spot size of ~20 μm, yielding a maximum power density greater than 10^16 W/m². The short pulse length has the additional advantage of creating an accurate starting point for the measurement of the ion flight times.

The HY1200 employed in this project has been specially modified to meet the requirements imposed by the application. If an external trigger pulse is given, indicating that a particle is available for analysis, the actual radiation pulse follows no later than 75 ns after the trigger (see also section 4.3.2). Such a short response time is not available with other laser types like pulsed N₂-lasers or excimer lasers. The latter can compete as far as peak power is concerned, but the beam characteristics can have a negative effect on the reproducibility of the resulting mass spectra.

102
4.3.2 Triggering of the HY1200

When the Nd:YAG laser is operated in the specially designed external trigger mode, the flash lamps are triggered at a fixed repetition rate of 10 Hz. In the internal trigger mode the Q-switch would be opened when the energy absorbed from the flash lamps reaches its maximum, after about 180 μs. However, with the modified circuitry an external trigger has to be provided to open the Q-switch. This trigger is generated by the electronics circuitry processing the photomultiplier signals. The Q-switch trigger pulse should be given roughly 180 μs after the synchronization pulse from the flash lamps, to avoid large variations in laser output energy. In practice a deviation of 20 μs from the nominal value is admissible, when a maximum jitter of 5% on the laser output energy is permitted. It should be stressed that the laser can only be fired within this 40 μs time window, which dramatically reduces the rate at which particles can be analyzed.

![Diagram of the trigger electronics](image)

Figure 4.2 Diagram of the trigger electronics

When a particle passes through the detection volume each photomultiplier tube (PMT) produces a signal with an amplitude of 300 μA at most. These signals are converted by the transimpedance amplifiers (1 mV/μA) and in addition amplified by a factor of 33. The signals produced in this way make up two of the three inputs of an electronic circuit, of which Figure 4.2 shows a schematic diagram. The third input is a synchronization pulse from the HY1200, indicating that the charging of the flash lamps is about to begin. The pulsed laser can only be fired when the flash lamps are fully charged. The time window within which this is the case follows after 160 μs, and is 40 μs wide. An output pulse at TTL level (8 μs wide) is generated whenever both discriminators simultaneously produce a pulse within the 40 μs time window. The output signal is fed to the Q-switch external trigger input, and after a delay of typically 75 ns the HY1200 emits it radiation pulse. The electronics add an extra 100 ns to the delay
time, yielding a total delay of approximately 175 ns. For a typical particle velocity of 200 m/s this implies that the particle moves over a distance of 35 μm before it is hit by the vaporization/ionization laser. It should be noted that this distance is of the same order of magnitude as the focal size of the HY1200, which is estimated to be approximately 20 μm. Figure 4.3 shows the timing sequence of detection and triggering events.

Figure 4.3 Timing sequence of the detection and triggering events. Note that the signals are not equally scaled.
4.3.3 Ion formation; experimental and model results

With the DVR model described in section 4.2.2 time constants and threshold irradiances can be calculated, which can be compared with the experimental parameters. Calculations are presented for water and carbon, which can be considered the most extreme cases of optically thin and thick particles. The adopted physical constants are listed in Table 4.1; most values are taken from Armstrong (1984), except for the ionization energies, which are ionization potentials taken from McLafferty (1980). The critical temperature of carbon was unknown, and a value of 5000 K was assumed. Analogous to Armstrong a 2 \( \mu \)m water droplet and a 1 \( \mu \)m carbon particle (diameters) were chosen as typical examples of optically thin and thick particles. It should be noted that for a quadrupled Nd:YAG laser (\( \lambda = 266 \) nm) the carbon particle is too large to be considered 'small', since \( \alpha = 12 \). In contrast, Armstrong performed his calculations for a CO\(_2\) laser (\( \lambda = 10.6 \) \( \mu \)m). This implies values for \( \alpha \) of 6 (20 \( \mu \)m diameter quartz particle) and 0.3 (1 \( \mu \)m diameter carbon particle) and it can be questioned whether the condition \( \alpha \ll 1 \) is satisfied. As a consequence the source function displays higher peak values, and the time constants and threshold irradiances are smaller than predicted.

**Table 4.1 Physical constants for water and carbon.**

<table>
<thead>
<tr>
<th>physical quantity</th>
<th>water</th>
<th>carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p ) (kg/m(^3))</td>
<td>1000</td>
<td>2250</td>
</tr>
<tr>
<td>( C ) (J/kg K)</td>
<td>4.19( \times )10(^3)</td>
<td>2.08( \times )10(^3)</td>
</tr>
<tr>
<td>( m ) (kg/mol)</td>
<td>1.8( \times )10(^{-2})</td>
<td>1.2( \times )10(^{-2})</td>
</tr>
<tr>
<td>( L_0 ) (J/kg)</td>
<td>2.25( \times )10(^6)</td>
<td>5.97( \times )10(^7)</td>
</tr>
<tr>
<td>( T_{cr} ) (K)</td>
<td>647</td>
<td>5000</td>
</tr>
<tr>
<td>( K ) (W/m K)</td>
<td>0.70</td>
<td>5.0</td>
</tr>
<tr>
<td>( c_0 ) (m/s)</td>
<td>1.5( \times )10(^3)</td>
<td>3( \times )10(^3)</td>
</tr>
<tr>
<td>( \kappa ) (m(^{-1}))</td>
<td>10(^5)</td>
<td>2( \times )10(^7)</td>
</tr>
<tr>
<td>( E_i ) (J/mol)</td>
<td>1.22( \times )10(^6)</td>
<td>1.09( \times )10(^6)</td>
</tr>
</tbody>
</table>

With the listed constants the characteristic times and threshold irradiances can be calculated for the two cases. The time constants, shown in Table 4.2, are in good agreement with the data from Armstrong. The article gives only one threshold irradiance (the \( L \) value for the water droplet: 3.4\( \times \)10\(^{13}\) W/m\(^2\)), but it proved impossible to produce the same result. However, as the results are in qualitative agreement, it is believed that the calculated irradiances give at least the order of magnitude of the thresholds involved. The results show that the thresholds for spontaneous vaporization and plasma formation are very similar for carbon particles.
In contrast, the fast heating region is believed to be significant for water droplets, as the two thresholds differ by two orders of magnitude. In this case the time constant for uniform heating of the δ zone (τ_δ) exceeds the laser pulse length and thus the DVR condition lasts for a time period t. The threshold irradiances for spontaneous vaporization and plasma onset are feasible with the HY1200 (10^{14}-10^{16} W/m^2) for both cases, which represent the extreme limits off the DVR model. From this it can be concluded that spontaneous vaporization and/or plasma formation can occur given the present experimental conditions.

Table 4.2 Characteristic times and irradiances for a 2 μm water droplet and a 1 μm carbon particle, calculated according to Armstrong (1984). Also listed are the plasma formation thresholds according to Armstrong (1984) and Vertes et al. (1989) (I_p and I thr, respectively).

<table>
<thead>
<tr>
<th>parameter</th>
<th>water droplet</th>
<th>carbon particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>τ_a (s)</td>
<td>6.7×10^{-10}</td>
<td>1.7×10^{-11}</td>
</tr>
<tr>
<td>τ_δ (s)</td>
<td>1.6×10^{-6}</td>
<td>5.8×10^{-10}</td>
</tr>
<tr>
<td>τ_σ (s)</td>
<td>1.6×10^{-6}</td>
<td>2.3×10^{-7}</td>
</tr>
<tr>
<td>I_{DVR} (W/m^2)</td>
<td>9.3×10^{11}</td>
<td>2.7×10^{12}</td>
</tr>
<tr>
<td>I_q (W/m^2)</td>
<td>1.4×10^{13}</td>
<td>1.6×10^{15}</td>
</tr>
<tr>
<td>I_p (W/m^2)</td>
<td>1.1×10^{18}</td>
<td>1.7×10^{15}</td>
</tr>
<tr>
<td>I_{thr} (W/m^2)</td>
<td>4.3×10^{13}</td>
<td>1.4×10^{14}</td>
</tr>
</tbody>
</table>

The plasma formation thresholds estimated with the hydrodynamic model from Vertes et al. (1989), described in section 4.2.3 are both significantly lower than the thresholds calculated using the DVR model from Armstrong (1984). Furthermore, it can be concluded that the irradiance used in the experiments (approximately 3×10^{14} W/m^2) is likely to cause plasma effects. This hypothesis is supported by the relatively high degree of ionization found in all experimental mass spectra (see also section 5.4.2). It should be stressed that neither model includes the influence of target dimensions on the plasma formation thresholds. It can be questioned whether one-dimensional models can adequately describe the interaction of radiation with an aerosol particle, but a more extensive description is complex, and no such model has been reported yet.

Only a small number of publications on the experimental determination of plasma formation thresholds can be found in literature. Most of these deal with laser induced air breakdown and cover only a limited parameter range. An exception is the paper published by Thomson and Murphy (1993). It lists ion and plasma formation thresholds for particles in vacuum, and different sizes, materials and wavelengths are included. Unfortunately, their definition of the plasma formation threshold is quite ambiguous, because it depends on experimental parameters such as the
ion detection limit and the detector saturation level. Furthermore, there is
a large absolute uncertainty (55 to 65 %) in the reported thresholds, which
are therefore expected to give only the order of magnitude. The results
indicate that the thresholds for ion and plasma formation decrease with
decreasing wavelength. For the excimer wavelengths (193, 248, 308 and
337 nm) the ion formation thresholds for 7 to 10 \( \mu \)m diameter oleic acid
and ammonium sulphate particles range from 2.5\( \times 10^{10} \) to 5.0\( \times 10^{11} \) W/m\(^2\),
corresponding to our definition of moderate to high irradiance. Plasma
formation thresholds could not be measured, but these are estimated to be
30 to 100 times greater. For the CO\(_2\)-laser (\( \lambda = 10.6 \) \( \mu \)m) ion formation starts
at 2.8\( \times 10^{12} \) W/m\(^2\), and plasma formation is likely for irradiances about a
factor two higher, exceeding 4.8\( \times 10^{12} \) W/m\(^2\). These results indicate that
ions are produced more easily with short wavelength radiation. It is
suggested that the plasma formation thresholds follow the same trend,
although the laser power was too low to confirm this experimentally.
Thomson and Murphy found an increase in the ion formation thresholds
with increasing particle size. In contrast, other experiments on air
breakdown limits indicate that ion formation becomes more difficult with
decreasing particle size (see e.g. Smith 1977). A possible explanation for
the findings of Thomson and Murphy could be the presence of absorption
centres (see also Appendix 4A). This effect increases with particle size,
resulting in lower threshold irradiances. It is not clear though why the air
breakdown limits are not influenced in a similar way.

As was to be expected, Thomson and Murphy found a strong increase in
the ion yield when passing the plasma formation threshold. Furthermore
they noticed a shift in the mass spectrum towards lighter ions, which is
characteristic of the recombination and fragmentation processes taking
place in the plasma. With the Nd:YAG laser used in the present study, the
intensity can roughly be varied from 10\(^{14} \) to 10\(^{16} \) W/m\(^2\). All mass spectra
were recorded at a nominal laser intensity of roughly 3\( \times 10^{14} \) W/m\(^2\), which
is higher than the plasma formation thresholds estimated by Thomson and
Murphy (1993). This implies that the laser pulse is likely to cause plasma
ignition and thus induce the formation of relatively small ions. The
recorded mass spectra, which will be discussed in detail in chapter 5, do
not reject this hypothesis.

Although plasma formation is desirable for the analysis of inorganic
compounds, it makes it impossible to obtain structural information on
organic compounds. It is therefore necessary to use a different laser,
operating at a lower pulse power. An adjustable beam attenuator will
increase the control of the intensity, which is likely to improve the mass
spectra. By using a different type of laser (for example an excimer laser)
it should be possible to make the triggering much simpler. As excimer
lasers are not pumped by flash lamps, synchronization with an internal
clock cycle is not necessary, and the analysis efficiency could be increased
by a factor of 2000. It has to be realized, though, that the delay from
trigger to output is longer for excimer lasers: about 1 to 2 \( \mu \)s. This subject
will be discussed further in the sections 5.4 and 5.5.
References


Kinetics of ion formation from salts by pulsed-laser irradiation, Int. J. Mass

Gas breakdown initiated by laser radiation interaction with aerosols and solid

Photo Ionization Time of Flight Mass Spectrometry Applied to Organic Molecules. PhD
thesis from the University of Amsterdam (UvA), Ch. 1.

Laser-induced ion formation thresholds of aerosol particles in a vacuum, Appl.
Opt. 32, 6818-6826.

Threshold conditions of plasma ignition in laser ionization mass spectrometry
of solids, Anal. Chem. 61, 1029-1035.

Hydrodynamic modelling of laser-plasma ionization processes, Int. J. Mass


Physics of shock waves and high-temperature hydrodynamics phenomena, Academic,
New York.

Explosive vaporization of a large transparent droplet irradiated by a high
Appendix 4A Absorption centres and morphology dependent resonance

The absorption of radiation by a particle and the subsequent conversion to heat are governed by the absorption cross section, also called the source function. The source function describes the absorption distribution within the particle, which in general is not uniform. In the case of homogeneous, spherical particles the source function can be approximated using Mie theory, as was already recognized by Kerker and coworkers (Dusel et al. 1979). In the case of large particles it is also possible to apply geometric optics, as was demonstrated by Jarzembski and Srivastava (1989). Figure 4A.1, taken from Greene et al. (1985), illustrates the influence of the size parameter $\alpha \equiv \pi d / \lambda$ for semi-transparent particles. Radiation propagates along the z-axis from negative, i.e. from left to right. The initial errors in figure labelling, pointed out by the authors themselves in 1988, have been corrected. The source function for small particles is uniform over the complete equatorial plane, indicating a homogeneous absorption of radiation. Regions of enhanced absorption arise with increasing size parameter, at the front and/or backside of the particle. The exact shape and location of these so-called absorption centres depend on the complex index of refraction, $N=n+ik$.

Figure 4A.1 The source function for $N=1.3-0.1i$ and different size parameters: a. $\alpha=0.5$, b. $\alpha=3$, c. $\alpha=10$ and d. $\alpha=20$ (taken from Greene et al. 1985).
The same paper also describes the influence of the complex refractive index. The real part of the index of refraction has only a moderate influence on the source function, shifting the maximum towards the centre of the particle for increasing values of \( n \). An increase in the imaginary part of the refractive index shifts the region of maximum absorption towards the surface of the particle, as illustrated by Figure 4A.2. It is for these cases that the approximation for 'optically thick' particles (Armstrong 1984) holds, provided \( \alpha \ll 1 \).

![Figure 4A.2](image)

Figure 4A.2 The source function for different values of the imaginary part of the refractive index taken from Greene et al. 1985). The calculations were performed for \( \alpha=5 \), and \( N=1.3-k \), with \( k=0.01 \) (a), \( k=0.1 \) (b), \( k=1 \) (c) and \( k=10 \) (d).

The occurrence of absorption centres has been confirmed experimentally by Pinnick and coworkers (1988, 1990). The observation of droplet explosions on either the irradiated or shadow side of the particle is in agreement with the calculated source functions. Furthermore it is shown, that in some cases the particle can function as an optical lens focusing the incident radiation onto a spot just outside the particle on the shadow side. In this case gas breakdown can start outside the particle, but the opposite is also possible. These observations were also reported by Hsieh et al. (1987).
A related phenomenon is known as morphology dependent resonance (MDR). From experiments in which particles were optically levitated (Pinnick et al. 1992) it was found that sharp minima in the breakdown thresholds occur for particle sizes satisfying a resonance condition. These results imply an enhanced absorption by these particles, caused by resonance effects. Although Mie theory predicts maxima in the source function as high as $10^5$ times the average value, the experiments yield much lower values. This difference could not be explained by Pinnick et al. (1992), but it is likely to result from assumptions in Mie theory which are not allowed in this case. MDR’s have also been observed in elastically scattered light, in fluorescence and in Raman spectra (Armstrong 1988). It should be stressed that resonance effects only play a role for spherical particles. Additionally the size parameter has to satisfy a resonance condition and very small deviations ($\Delta \alpha / \alpha = 10^{-5}$) have been found to be significant. In conclusion it can be said, that MDR’s are in general insignificant, but that absorption centres are likely to play a role.
5.1 Introduction

The subject of this chapter is time-of-flight mass spectrometry (tof-ms). The short ion burst produced by the laser-ionization process described in chapter 3 has to be analyzed if the chemical composition of a particle is to be determined. Time-of-flight mass spectrometry is by far the most suitable analysis technique available for analyzing the ions produced from an aerosol particle. Firstly, it provides a complete mass spectrum for every ion burst, in contrast with scanning mass spectrometers from, for example, the quadrupole type. Both positive and negative ions can be measured, but in the present study only spectra from positive ions were measured. Secondly, the technique is very sensitive, and spectra can be obtained for very small amounts of sample approaching the attomole level. This feature makes tof-ms extremely suitable for analyzing aerosol particles. Thirdly, the mass range measurable with a tof-ms is theoretically unlimited, which enables the analysis of large molecules like proteins and polymers. If the instrument is to be applied to organic substances, ion masses in the order of 500 Da have to be resolved.

Section 5.2 gives a brief description of the technique, including the basic equations involved. Part of this section will deal with mass resolution and some of the methods available to improve it. The remainder of the chapter is devoted to the experiments performed within the scope of this thesis. After a brief description of the experimental setup and procedure (section 5.3) the results will be discussed in section 5.4.

5.2 Theory of operation

Ion separation in a time-of-flight analyzer results from the mass dependence of the flight time of ions starting at the same time and position within an electrostatic field. The one-dimensional motion of a body undergoing an external force is in general described by

$$\frac{dx}{dt} = \frac{d^2x}{dt^2} t$$

Gravitation and friction forces can be neglected when an ion moves within an electrostatic field in vacuum, leaving just the influence of the potential difference ($\Delta V$) applied over a distance $L$. 
\[ \frac{d^2 x}{dt^2} = \frac{ze \Delta V}{L m} \] (5.2)

It is assumed that the ion carries \( z \) elementary charges (\( e \)) and that its mass (\( m \)) does not change in time. For a given setup the electrode separation and the applied potentials are known, and Equation 5.1 can be integrated over every part of the flight path. The total flight time of an ion can be found by calculating the sum of all the sections involved. In general, the flight path consists of one or two acceleration sections, a field-free region without an applied potential difference, and an accelerating zone in front of the ion detector. In some cases an electrostatic mirror, usually called reflectron, is applied to enlarge the flight path and enhance mass resolution and this technique will be discussed later. A rough estimate of the ion flight time can be obtained from an energy balance, assuming that all potential energy stored in the electrostatic field is converted to kinetic energy. This approach yields the following expression for the flight time \( t_{\text{flight}} \):

\[ t_{\text{flight}} L \sqrt{\frac{1}{2 \Delta V}} \sqrt{\frac{m}{ze}} \] (5.3)

which clearly shows that the flight time is approximately proportional to the square root of the mass to charge ratio.

The mass resolution of a conventional linear time-of-flight instrument is poor in comparison with quadrupole mass spectrometers: \( m/\Delta m = 100-300 \), where \( \Delta m \) is defined as the mass difference that can just be distinguished at mass \( m \). There are three factors that broaden the flight time profiles (Boesl et al. 1994):

1. The ions are generated over a time interval, of which the length is determined by the temporal profile of the laser pulse. This purely temporal effect causes broadening in the order of the laser pulse length (10 ns in the case of the Lumonics HY1200).
2. The ionization volume has finite dimensions. In most cases these dimensions are determined by the laser focus size, but since the sample itself is very small in aerosol analysis, particle size dominates here. The initial spatial distribution of the ions in the ion source results in different potential energies, causing differences in flight time. The spatial distribution also results in a difference in flight path, which is a second factor affecting the ion flight time. Apart from this, it should be noted that particles can be ionized at different positions within the laser focus. This effect does not affect resolution, but it causes the complete flight-time spectrum to shift.
Ions can have an initial velocity prior to acceleration, either because the sample itself is moving or because the ionization process produces kinetic energy. Analogous to the factor described under 2, this effect can be separated into a pseudo-temporal and a pseudo-spatial component. In linear instruments with a perpendicular supersonic beam inlet the spatial effect usually dominates over the temporal effect, which is often called the 'turn around time effect'. As with the previously mentioned factors, the spread in ion kinetic energy results in a broadening of the tof profiles.

The listed problems were already recognized when time-of-flight mass spectrometers were introduced in the 1950s, and several solutions have been applied successfully since. The finite time of ion formation (1) can be minimized by using a laser with a short pulse length. Modern Q-switched and mode-locked lasers have made peak broadening due to this factor an effect of minor importance. The two spatial effects (2) are correlated and can compensate for each other at a certain point within the field-free region: the so-called space focus. At this point, the decrease in flight-time due to the larger velocities of ions formed at higher potential energies is compensated for by the increase due to the longer acceleration path. When the acceleration region is subdivided into two parts with different electric fields (three electrode, two-stage ion source), the position of the space focus can be shifted by varying the field strength ratio (Wiley and McLaren 1955). Differences in kinetic energy (3) are best compensated with a reflectron, originally developed by Mamyrin (1966). The simplest type is the one-stage reflectron shown in Figure 5.1, but two-stage versions are also available.

![Figure 5.1 Time-of-flight focusing in a homogeneous field by a one-stage reflector. The reflectron potential $U_R$ is applied to the electrodes by a voltage divider.](image)

115
The working principle of reflectrons is best illustrated by considering ions of one distinct mass and no spatial or temporal distribution, but with different kinetic energies. After leaving the field-free region, ions with higher kinetic energy enter the ion mirror first, followed by those with lower kinetic energy. The former penetrate deeper into the reflecting field than the latter, resulting in a longer residence time within the reflector. By choosing the appropriate potentials and geometry the shorter flight time of high energy ions within the field-free region is compensated for by a longer residence time within the reflector. As a result, all ions of the same mass will arrive at the detector simultaneously. The contribution of turn around times to the spread in flight time can be reduced by high extraction fields. In summary, the ion peak width results from the turn around time, higher-order energy compensation terms not compensated for by the reflectron, and intrinsic time spreads (for example ion formation time and detector characteristics). If the listed methods are carefully applied, mass resolution can be increased up to $10^5$ or higher.

An alternative approach uses time dependent acceleration of the ions, in addition to the two-stage ion source described earlier. With this method called post-source pulse focusing (PSPF, see e.g. Grundwürmer et al. 1994), differences in ion formation times $1$ and initial ion velocities $3$ can be compensated. The ions produced in a conventional two-stage electric field enter a short, initially field-free pulse-focusing region. After the ions have entered a voltage is applied to this region, compressing the individual mass ion packets. As a result, the resolution of the ion signal at the detector is higher. With this technique a mass resolution of $4600$ has been achieved for ions with a mass of $656$ Daltons.

5.3 Experimental setup

The time-of-flight mass spectrometer used in this project was custom built by the "Institut für Lasermedizin" at the Heinrich-Heine-University in Düsseldorf, Germany. Figure 5.2 schematically shows the components making up the mass spectrometer (next page). Particles from the aerosol beam generator (1) enter the first stage of a two-stage ion source (2), where they are hit by a pulse from the vaporization/ionization laser (not shown in the figure). The pulsed laser is operated at its lowest power, where every pulse contains approximately $1$ mJ of energy. The applied electrostatic fields move positive ions formed from the particle towards the flight tube of the mass spectrometer. Vertically placed electrodes (3) enable steering of the ion beam in the horizontal plane and similarly vertical steering is achieved by the deflector plates (4). The tof-ms is equipped with a single-stage reflectron (5), but a detector (6) placed behind the reflectron makes it also possible to measure in a linear mode (with all reflectron stages connected to earth). When working in the reflectron mode ions are analyzed with a second detector (7), placed at the opposite end of the flight tube. In the experiments described in this thesis the tof-ms was operated without the reflectron.
One single set of potentials was used in all experiments. The back electrode of the three-electrode, two-stage ion source was maintained at +6 kV. This relatively high acceleration potential minimizes the influence of turn around time effects. The optimal potential for the first acceleration electrode was found to be +4 kV, and the second electrode was connected to earth. The distance separating each electrode pair is 1 cm. In the present experiments it was not necessary to manipulate the ion beam in the horizontal plane, and therefore both the left and right ion lens were connected to earth. The (vertical) deflector plates had a small influence on the resulting spectra, and voltages ranging from 200 to 300 V were applied to the upper plate. The field-free region of the tof-ms is approximately 1.10 m long, measured from the second acceleration electrode to the detector assembly. The detector contains a post-acceleration region (2.8 cm long), maintained at -2 kV. The ion signal is multiplied by a set of two microchannel plates, measured by a detector and subsequently stored on a digital oscilloscope. Flight-time spectra are typically recorded during 20 μs at a sampling frequency of 100 megasamples per second.

Because of the low duty cycle of the vaporization/ionization laser it was necessary to generate aerosols with a high particle concentration for calibration and testing. For this purpose an ultrasonic air humidifier (Robeson model 3007) was converted into an aerosol generator by adding a drying section. Particle drying is achieved by raising the temperature of the aerosol, passing it through a packed bed of silica particles, and adding dry dilution air. Test aerosols were generated from concentrated solutions (approximately 10 vol%) of the following compounds:

1 NaCl (140 g/l)
2 a mixture of NaCl (100 g/l), KCl (30 g/l) and (NH₄)₂SO₄ (70 g/l)
3 (NH₄)₂SO₄ (175 g/l)
4 ascorbic acid (100 g/l)
The concentration of the resulting aerosols was so high that it could not be measured directly. From the rate at which the pulsed laser was fired (about 1 Hz) it is estimated that the particle concentration at the inlet was in the order of $10^5$/m$^3$. The particle size distribution is wide and ranges from smaller than 0.5 μm to 7 μm, with a mean diameter at approximately 4 μm.

5.4 Experimental results

5.4.1 General discussion

With the experimental setup described in the previous section it proved possible to record spectra from single particles for each of the four test aerosols. Examples of these spectra are reproduced in Appendix 5A. The particle concentration was high enough as to result in a satisfactory trigger rate of approximately once per second. Not every shot from the Nd:YAG laser produced a usable mass spectrum; about 90 % of the recorded signals contained no significant peaks at all. This problem is most likely caused by imperfections in the alignment of the detection and ionization laser beams, which was extremely difficult to achieve in practice. Alignment of the detection laser was realized by suspending a thin nylon line through the nozzle and skimmers, after which the photomultiplier signal was maximized by moving the laser focus. The ionization laser was aligned with the aid of a small piece of burn paper, which was slowly moved across the focal plane of the detection laser while firing the ionization laser at a fixed repetition rate. The focus of the Nd:YAG laser beam was shifted until the burn marks from the two lasers completely overlapped. A disadvantage of the described alignment method is that it is not possible to check whether the two laser beams are positioned coaxially. If this is not the case, as illustrated by Figure 5.3, some of the particles passing through the detection volume are missed by the pulse from the Nd:YAG laser. An alternative explanation for the low hit rate can be sought in a difference in spot size between the two lasers. Calculation of a theoretical focal size for the Nd:YAG laser using the ABCD law (Appendix 2A) is not possible, because beam divergence and diameter are not known for the frequency quadrupled radiation. Burn marks on the photo paper suggest a focal size in the order of 20 μm, which is comparable to the focus diameter calculated for the helium-neon laser beam (16.4 μm). It should be mentioned that it is difficult to obtain estimates of the focal sizes achievable in practice.

[Figure 5.3 Exaggerated sketch of angular misalignment. Particles passing through the detection volume will be detected, but only those passing through the overlap region will also be hit by the ionization laser.]
Most spectra recorded for the sodium chloride particles are usable; about 10% of the signals are not. Peaks in these spectra are much wider due to detector saturation, and interpretation is difficult. Typical examples of a good and a saturated spectrum are shown in Figure 5.4.

Figure 5.4 Examples of a good NaCl spectrum (a) and a spectrum displaying detector saturation (b).
The time scale has been converted to a mass scale using the equation

\[
\frac{m}{z} = \left( \frac{t-c_2}{c_1} \right)^2
\]  

(5.4)

in which \( t \) is the ion flight time and \( c_1 \) and \( c_2 \) are experimentally determined calibration constants. \( m/z \) is the ratio of the ions mass (in Daltons) over its charge (number of elementary charges). One Dalton (=one Atomic Mass Unit or A.M.U.) is defined as 1/12th part of the mass of the \(^{12}\text{C} \) isotope. In the case of the sodium chloride spectra the calibration constants \( c_1 \) and \( c_2 \) were found to be \( 1.15 \times 10^{-6} \) s/Da\(^{1/2} \) and \( 2.37 \times 10^{-7} \) s respectively. It is believed that the saturation effects occur when the intensity of the pulsed laser is relatively high. The laser intensity displays a substantial shot to shot variation due to the triggering procedure, and furthermore particles are hit at different positions within the spatial intensity profile. An alternative explanation relates saturation effects to particle size. Sinha and Friedlander (1985) have shown that the integrated ion signal can be related to the total amount of sodium present in a particle, and thus - for a given concentration - to the particle mass. Unfortunately, the setup did not allow for monodisperse aerosols to be measured, and therefore the influence of particle size could not be clarified. The cluster ions found in the good spectra ((Na)_2\(^+ \) and (Na,Cl)(\^+); masses 46 and 81/83) are quite common in spectra from alkalihalides. Under optimal conditions, it should also be possible to detect heavier clusters, for example those containing three sodium and two chlorine ions. These cluster ions can also be found in sodium chloride spectra recorded with a LAMMA instrument (Marijnissen et al. 1988).

Mass resolution is commonly defined as the largest mass, for which two adjacent masses are essentially completely separated. However, because the mass resolution defined in this way is difficult to determine in practice, an alternative definition was adopted. The mass resolution \( m/\Delta m \) was calculated from the (Na,Cl)(\^+) peaks, using the relation \( m/\Delta m = t/4\Delta t \). The temporal peak width is assumed to be \( 2\Delta t \) and the width of a peak in the mass spectrum is twice as large (see Equation 5.3). The standard deviation \( \Delta t \) is calculated over a time interval of 100 ns length - which always exceeds the total width of a peak - from:

\[
\Delta t = \sqrt{\frac{\sum_i (t_i - \bar{t})^2 V_i}{\sum_i V_i}}
\]  

(5.5)

In this equation \( V_i \) represents the \( i \)th signal voltage (at \( t=t_i \)) and \( \bar{t} \) is the peak centre, found from

\[
\bar{t} = \frac{\sum_i t_i V_i}{\sum_i V_i}
\]  

(5.6)
The average value of the mass resolution for all good NaCl spectra is 110. This value is too low for analyzing organic substances, in which case a mass resolution of 500 is desirable. It should be noted that the resolution would be approximately 20% higher if it had been based on the full width at half maximum (FWHM), as suggested by Grundwürmer et al. (1994). This approach has not been adopted because the agreement with the conventional definition of mass resolution is not as good.

5.4.2 Degree of ionisation

Sodium chloride is a material which is already composed of ionized species, which are relatively easy to volatilize. The same can be said about potassium chloride. It was therefore not surprising that ions were readily formed when particles of these materials were sent into the instrument. It was unexpected though, that the particles containing NaCl, KCl and (NH₄)₂SO₄ did not produce any significant signals from the third compound, ammonium sulphate. Spectra from these mixed particles, of which Figure 5.5a gives an example, did hardly ever display peaks that could be attributed to ammonium sulphate. In contrast, experiments with pure ammonium sulphate particles did produce proper mass spectra (Figure 5.5b, next page). This observation indicates that the compounds are not homogeneously distributed, or that the formation of ions from ammonium sulphate is suppressed by the more easily ionized alkalihalides (matrix effects).

![Mass spectrum](image)

Figure 5.5a Mass spectrum from a particle composed of a NaCl/KCl/(NH₄)₂SO₄ mixture.
After the successful analysis of inorganic species, we tried to analyze organic particles. Numerous mass spectra were obtained for particles composed of ascorbic acid, generally known as vitamin C. The spectra, of which an example is shown on the next page as Figure 5.6, reveal that the generated ions are highly fragmented. The spectrum measured with a conventional quadrupole mass spectrometer (ionization by electron impact) displays a molecular ion peak at mass 176, and strong peaks at masses 43, 85, 116 (highest peak) and 119 (Davies et al. 1991). In contrast, the spectra obtained in the present study contain no significant peaks above mass 80, and very intense peaks from ions like CH$_3^+$ (15), H$_3$O$^+$ (19), C$_2$H$_5^+$ (29), and CH$_3$O$^+$ (31). Na$^+$ (23) is present as an impurity. From these observations it can be concluded that laser-ionization with an intensity in the order of $3\times10^{14}$W/m$^2$ (estimate based on a pulse energy of 1 mJ and a focal diameter of 20 µm) produces much stronger fragmentation than conventional ionization by electron impact. The model calculations presented in chapter 4 suggest that plasma formation is possible with the applied intensity, which could be an explanation for the observed fragmentation.
5.4.3 Reproducibility

If the instrument is to be applied successfully, it is essential that the mass spectra are reproducible. There are several ways according to which reproducibility can be quantified, and this section will discuss three alternatives. First the variability of the peak position and peak area will be analyzed and finally the correlation between the peaks in a spectrum will be examined.

Peak positions were determined in 30 good spectra recorded for the sodium chloride particles, using the definition given by Equation 5.6. In every spectrum the positions of the peaks with masses 23, 46, 81 and 83 were determined, after which the averages and standard deviations were calculated. The standard deviations for the four collections of peaks were all in the order of 16 ns, which roughly corresponds to 0.2 Dalton at mass 83. The spread in peak position can be caused by a number of factors:

1. Particles can have different positions within the electric field when they are hit by the laser pulse, which results in a systematic shift in starting position for all ions. Furthermore it was noticed that the electrode grids were damaged, causing inhomogeneity in the electric fields and thus a spread in the ion flight time.

2. Due to the nature of the laser-induced fragmentation process the kinetic energy of the ions formed varies from shot to shot. This effect influences the ion flight time.
Temporal jitter in the electronics of either the laser or the triggering circuit, directly influences the flight-time spectra. Of the three factors listed above only the first one can be dealt with. Repair of the damaged grids will obviously result in a more homogeneous electric field, and thus reduce the spread in peak position. Additional improvements can be expected from decreasing the focal size of the vaporization/ionization laser.

Figure 5.7 Histograms showing the distribution of the deviation from the mean peak area, reproduced from Marijnissen et al. (1988) (a), and calculated for the present work (b).
An attempt to quantify reproducibility was employed by Marijnissen et al. (1988). In this case the areas of a number of peaks in a collection of LAMMA spectra were determined, which were next normalized with regard to their average values. The distribution of the deviation from the mean was plotted in a histogram, and the result is reproduced on the previous page as Figure 5.7a. The described procedure was also applied to the sodium chloride spectra obtained with the present setup and the results are shown in Figure 5.7b. The figure shows that our setup generates spectra which are slightly less reproducible than those obtainable with a LAMMA-500. The standard deviations (38 and 48 % for the old and new results respectively) indicate that the results are comparable as far as reproducibility is concerned. This was not expected beforehand, as the amount of energy deposited in a particle in the new experiments is likely to vary substantially. It is likely that the reproducibility can be improved further through optimization of the ionization process and fine-tuning of the mass spectrometer. Finally, it should be mentioned that the mass spectra obtained in the present study are recorded for particles from a wide size distribution, and that a 10 % spread in laser energy was permitted. Both factors influence the reproducibility of the spectra, but up to what extent is unknown.

Some additional information on the reproducibility can be obtained by analyzing the correlation between the peaks present in a spectrum. A standard way of doing this is by constructing the correlation matrix, which gives a measure for the relations between any number of selected parameters. In this study it was decided to use peak area as the parameter for the correlation matrix. Peak areas were determined for the 9 strongest peaks in 26 NaCl/KCl/(NH₄)₂SO₄ spectra and Table 5.1 lists the masses and ion structures.

Table 5.1 Masses and ion structures for the 9 peaks used to construct the correlation matrix.

<table>
<thead>
<tr>
<th>peak number (k)</th>
<th>ion mass (Dalton)</th>
<th>ion structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23</td>
<td>Na⁺</td>
</tr>
<tr>
<td>2</td>
<td>39</td>
<td>39K⁺</td>
</tr>
<tr>
<td>3</td>
<td>41</td>
<td>41K⁺</td>
</tr>
<tr>
<td>4</td>
<td>46</td>
<td>(Na₂)⁺</td>
</tr>
<tr>
<td>5</td>
<td>62</td>
<td>(Na₃⁹K)⁺</td>
</tr>
<tr>
<td>6</td>
<td>81</td>
<td>(Na₂⁺Cl)⁺</td>
</tr>
<tr>
<td>7</td>
<td>83</td>
<td>(Na₂⁺Cl)⁺</td>
</tr>
<tr>
<td>8</td>
<td>97</td>
<td>(Na₃⁹K⁺Cl)⁺</td>
</tr>
<tr>
<td>9</td>
<td>99</td>
<td>(Na₃⁹K⁺³⁵Cl)⁺ or (Na₄¹K⁺³⁵Cl)⁺</td>
</tr>
</tbody>
</table>
From the calculated peak areas a data matrix $X$ was constructed
\[
\begin{pmatrix}
x_{11} & \cdots & x_{19} \\
\vdots & \ddots & \vdots \\
x_{261} & \cdots & x_{269}
\end{pmatrix}
\] (5.7)

The 81 elements of the correlation matrix are defined by
\[
r_{jk} = \frac{\sum_{i=1}^{26} (x_{ij} - \bar{x}_j)(x_{ik} - \bar{x}_k)}{\sqrt{\sum_{i=1}^{26} (x_{ij} - \bar{x}_j)^2 \sum_{i=1}^{26} (x_{ik} - \bar{x}_k)^2}}
\] (5.8)

where $\bar{x}_j$ and $\bar{x}_k$ represent the mean values of the columns $j$ and $k$ (see e.g. Brereton 1992). In order to evaluate the results some kind of estimate of the error is needed, and according to Milton and Arnold (1986) a 95% confidence interval on the estimated correlation coefficient $r_{jk}$ can be calculated from
\[
\text{lower bound} = \frac{(1+r_{jk}) - (1-r_{jk})\exp \left( \frac{-2\cdot1.96}{\sqrt{n-3}} \right)}{(1+r_{jk}) + (1-r_{jk})\exp \left( \frac{-2\cdot1.96}{\sqrt{n-3}} \right)}
\] (5.9)

and
\[
\text{upper bound} = \frac{(1+r_{jk}) - (1-r_{jk})\exp \left( \frac{-2\cdot1.96}{\sqrt{n-3}} \right)}{(1+r_{jk}) + (1-r_{jk})\exp \left( \frac{-2\cdot1.96}{\sqrt{n-3}} \right)}
\] (5.10)

In these expressions $n$ represents the number of observations, which is 26 in our case. Applying these equations to our data set yields the following (symmetrical) correlation matrix, in which the lower and upper limits of the 95% confidence interval are represented by sub- and superscripts respectively:
\[
\begin{pmatrix}
1 & 0.64^{0.082}_{0.034} & 0.66^{0.083}_{0.037} & 0.52^{0.076}_{0.017} & 0.42^{0.069}_{0.004} & 0.22^{0.056}_{0.018} & 0.23^{0.057}_{0.017} & 0.31^{0.062}_{0.009} & 0.31^{0.062}_{0.009} \\
... & 1 & 0.86^{0.094}_{0.071} & 0.73^{0.087}_{0.046} & 0.62^{0.081}_{0.030} & 0.53^{0.076}_{0.017} & 0.54^{0.077}_{0.020} & 0.66^{0.083}_{0.036} & 0.63^{0.082}_{0.032} \\
... & ... & 1 & 0.80^{0.091}_{0.059} & 0.70^{0.086}_{0.043} & 0.56^{0.078}_{0.022} & 0.57^{0.078}_{0.023} & 0.64^{0.083}_{0.034} & 0.65^{0.083}_{0.035} \\
... & ... & ... & 1 & 0.87^{0.094}_{0.072} & 0.83^{0.092}_{0.066} & 0.81^{0.091}_{0.062} & 0.85^{0.093}_{0.069} & 0.83^{0.092}_{0.066} \\
R = & ... & ... & ... & ... & 1 & 0.76^{0.088}_{0.052} & 0.78^{0.090}_{0.057} & 0.86^{0.093}_{0.070} & 0.85^{0.093}_{0.069} \\
... & ... & ... & ... & ... & 1 & 0.96^{0.098}_{0.091} & 0.87^{0.094}_{0.072} & 0.87^{0.094}_{0.073} \\
... & ... & ... & ... & ... & ... & 1 & 0.84^{0.093}_{0.068} & 0.85^{0.093}_{0.069} \\
... & ... & ... & ... & ... & ... & ... & 1 & 0.97^{0.099}_{0.094} \\
... & ... & ... & ... & ... & ... & ... & ... & 1 
\end{pmatrix}
\]

Analysis of the calculated matrix leads to a number of observations:

1. The area of the $^{25}$Na$^+$ peak shows no significant correlation with the $^{81}$(Na$_2$Cl)$^+$, $^{83}$(Na$_2$Cl)$^+$, $^{97}$(NaKCl)$^+$ and $^{99}$(NaKCl)$^+$ peaks, as 0 lies within the 95% confidence interval for these cases. This result can be explained by noting that a high Na peak corresponds to strong fragmentation, in which case the formation of cluster ions is less likely.

2. There is a strong correlation between the peak pairs $^{81}$(Na$_2$Cl)$^+$ and $^{83}$(Na$_2$Cl)$^+$ ($r_{83}=0.96$), and $^{97}$(NaKCl)$^+$ and $^{99}$(NaKCl)$^+$ ($r_{99}=0.97$). This observation was to be expected, because in both cases the ions differ only in their isotopic composition. The fact that the correlation between the two potassium isotopes ($r_{93}=0.86$) is much weaker is most likely caused by the high amplitude of the $^{39}$K signal, which frequently exceeded the dynamic range of the detection equipment. The signal truncation resulting from this effect has probably disturbed the inherent correlation between the two isotopes.

3. The overall correlation found in this data set is high. This suggests that the peak areas of the considered peaks respond as a collective to disturbances like variations in particle size or laser intensity.

### 5.5 Conclusions

As described in the previous sections, it proved possible to record mass spectra from single particles with the developed instrument. At present a mass resolution of 110 at mass 83 has been demonstrated, which is too low to make the recognition of organic compounds feasible. It is expected that the resolution will be improved by optimization of the operating parameters and by utilizing the reflectron. Spectra were recorded for both
inorganic and organic substances. The reproducibility of the NaCl spectra is comparable to the results of Marijnissen et al. (1988), obtained with a LAMMA-500. Good spectra were recorded from pure (NH₄)₂SO₄ particles, but no peaks could be ascribed to this compound when analyzing mixed particles containing NaCl, KCl and (NH₄)₂SO₄. This result indicates that matrix effects can occur. The mass spectra from an organic compound (ascorbic acid) display predominantly small ions, probably due to plasma effects. The intensity of the vaporization/ionization pulse is estimated to be $3 \times 10^{14}$ W/m$^2$, which is often sufficiently high to cause plasma ignition (see also section 4.3.3). Although plasma formation is desirable for the analysis of inorganics, it makes obtaining structural information on organic compounds difficult. This problem can be solved by using a different laser type (either nitrogen or excimer), with a lower pulse energy. Additionally, the application of a vibrating orifice aerosol generator becomes feasible, and the shot-to-shot reproducibility is better. The present alignment method is too laborious and too complex; if the instrument is to be applied for routine measurements improvements are a prerequisite.

References


Appendix 5A Selection of mass spectra.

Four spectra are plotted for each of the four test aerosols; two good spectra (a and b), one spectrum displaying saturation effects (c), and one spectrum with a low ion current (d).

The four test aerosols were generated from solutions of the following compounds:

1. NaCl (140 g/l)
2. a mixture of NaCl (100 g/l), KCl (30 g/l) and (NH₄)₂SO₄ (70 g/l)
3. (NH₄)₂SO₄ (175 g/l)
4. ascorbic acid (100 g/l)
Figure 5A.2 Mass spectra from NaCl/KCl/(NH₄)₂SO₄ particles.
Figure 5A.3 Mass spectra from (NH$_4$)$_2$SO$_4$ particles.
Figure 5A.4 Mass spectra from ascorbic acid particles.
Summary and conclusions

Aim of this project is to develop an on-line instrument, capable of measuring the size and chemical composition of single aerosol particles. Possible applications include monitoring aerosol reactors and studying atmospheric chemistry. The main conclusion from this thesis is that a operational prototype has been built and tested. It uses a three stage vacuum system to generate an aerosol beam with a low divergence angle and a high transmittance. The pressure is reduced sufficiently to allow the application of a time-of-flight mass analyzer. The aerosol beam is probed in the analysis section by the focused beam of a low-power helium-neon laser. Every particle crossing the laser beam scatters light, which is detected by two photomultiplier tubes, mounted at angles of 45 and 90°. The signal is stored when both detectors produce a pulse simultaneously, and this event triggers the chemical analysis cycle. A pulsed Nd:YAG laser vaporizes the particle and generates ions, which are next analyzed by a time-of-flight mass spectrometer. In this way combined information on the size and the composition of the particle is obtained.

The aerosol beam generator developed as the inlet of the instrument effectively transports particles to the analysis section. The initial divergence angle for 1 μm PSL particles is 5x10^{-4} sterad, measured directly behind the nozzle. The transport efficiency varies with particle size, and values exceeding 90 % have been demonstrated. It is shown that particles with a diameter close to 1 μm are best sampled using a straight nozzle geometry (B in Figure 2.4). For particles larger than 2 μm a convergent nozzle geometry (A in Figure 2.4) has the highest transport efficiency. With a nozzle diameter of 0.3 mm the pressure at the ion source can be reduced to 3x10^{-4} Pa, which is low enough to operate the time-of-flight mass spectrometer. The sample flow rate is approximately 0.9 l/min. It can be worthwhile to apply sheath air to prevent the nozzle and skimmers from clogging, especially when analyzing high-concentration aerosols.

The optical setup enables the detection of particles down to 0.364 μm, and the ultimate detection limit is expected to be even lower. The use of two detectors prevents the occurrence of false triggers caused by dark spikes, found with every photomultiplier. Interpretation of the light scattering signals in terms of particle size is only partly possible. It was found that the laser intensity profile causes too much variation in signal width and amplitude to make these parameters readily interpretable. In contrast, the ratio of the two signal areas measured for a particle is independent of the laser intensity profile, but difficult to use because of the oscillating nature of the light scattering phenomenon. Therefore, adaption of the light scattering setup is necessary if a good estimate of particle size is to be obtained. The simplest solution is to reduce the detection volume, thus creating a more uniform illumination intensity. An alternative approach involves applying two laser beams, in which case the measurement of a particle’s flight time yields its aerodynamic diameter. A second alternative is using a lamp instead of a laser. This will reduce oscillations because of the averaging over the emitted spectrum.
It is possible to use the scattering signals to trigger the vaporization and ionization laser and produce mass spectra. About 10% of the laser pulses produce a usable mass spectrum and alignment errors are most likely significant. As a consequence, improvement of the alignment procedure is necessary. At present only high-concentration aerosols can be measured, because the internal clock cycle of the applied laser limits the analysis rate. This problem can be solved by using a different type of laser. Unlike Nd:YAG lasers, nitrogen and excimer lasers do not have flash lamps, which implies that they can be triggered at any given moment. The use of one of these laser types can raise the analysis efficiency by a factor of 2000.

The intensity of the vaporization/ionization pulse is estimated to be in the order of $3 \times 10^{14}$ W/m². According to model calculations, this is often high enough to cause plasma formation. The recorded mass spectra support this hypothesis, as they display a high degree of fragmentation. An adjustable beam attenuator will increase the control of the ionization process in future experiments. This is expected to improve the mass spectra, especially for organic species.

Mass spectra have been recorded for laboratory generated aerosol particles consisting of NaCl, KCl, (NH₄)₂SO₄, a mixture of these three salts, and ascorbic acid. The mass resolution is typically 110 at mass 83, which is too low for future applications. It is expected that the resolution can be increased substantially by optimization of the electrode potentials and by operating the mass spectrometer in the reflectron mode. The positions of the peaks in the spectra are fairly reproducible, with a standard deviation of 16 ns. The spread in peak position is unlikely to cause misinterpretation for masses smaller than 600. The peak area is less reproducible (standard deviation 48%), but yet it seems to reflect the relative composition of the particle. Good spectra were recorded from pure (NH₄)₂SO₄ particles, but no peaks could be ascribed to this compound when particles containing NaCl, KCl and (NH₄)₂SO₄ were analyzed. This result indicates that matrix effects can play a role.
Samenvatting

De lucht om ons heen bevat talloze deeltjes die grofweg tussen 0.1 en 10 micrometer groot zijn, zowel van natuurlijke als van menselijke oorsprong. In veel gevallen is het nuttig te weten hoe groot die deeltjes precies zijn, en welke stoffen zij bevatten. Dit is bijvoorbeeld interessant bij het onderzoek naar luchtverontreiniging, maar het is ook van belang bij de produktie van materialen in poedervorm. Dit proefschrift beschrijft de ontwikkeling van een nieuw instrument om de grootte en chemische samenstelling van afzonderlijke deeltjes te meten, waarbij tot tien deeltjes per seconde geanalyseerd kunnen worden. Het belangrijkste resultaat van het onderzoek is dat er een werkend prototype is gebouwd, dat nog wel op enige punten verbeterd kan worden.

Het apparaat zuigt lucht met deeltjes (het aërosol) door een kleine opening van enkele tiende millimeters. Door de lucht onder een scherpe hoek te laten stromen worden de deeltjes afgescheiden en ontstaat er een bundel van deeltjes. Deze deeltjesbundel zorgt ervoor dat de deeltjes één voor één de meetsector bereiken, waar ze de lichtstraal van een zwakke laser passeren. Elk deeltje zal het (zichtbare) licht van de laser in alle richtingen verstrooien, en de hoeveelheid verstrooid licht is een maat voor de grootte van het deeltje. Wanneer er een deeltje gedetecteerd wordt gaat er onmiddellijk een signaal naar een tweede laser, die na een zeer korte tijd een krachtige, ultraviolette lichtpuls uitzendt. Deze puls zorgt dat het deeltje uiteenvalt, waarbij onder andere geladen fragmenten (ionen) ontstaan. Een elektrisch veld zorgt dat de ionen een rechte buis in getransporteerd worden, waar ze uiteindelijk een detector bereiken. De tijd die de ionen nodig hebben om dit traject af te leggen hangt af van hun massa, en op deze manier wordt informatie verkregen over de chemische samenstelling van het deeltje.

Het onderdeel dat de deeltjesbundel produceert werkt efficiënt. De divergentie van de bundel, die transportverliezen veroorzaakt, is gering: 0.7° voor deeltjes van 1 μm. Hierdoor bereiken de meeste deeltjes de analysesectie, en de gemeten efficiëntie is hoger dan 90%. Er zijn twee verschillende soorten spuitmonden onderzocht: rechte en convergente (geometrie A en B in figuur 2.4). Het blijkt dat B het meest geschikt is voor deeltjes van circa 1 μm. terwijl A beter voldoet voor deeltjes groter dan 2 μm. Wanneer de diameter van de spuitmond 0.3 mm is wordt in de analysesectie een druk van 3×10⁻⁹ bar bereikt. Het aangezogen debiet is dan circa 0.9 l/min. Om bij hoge concentraties verstopping te voorkomen kan het nuttig zijn de deeltjesbundel af te schermen met een laagje gefilterde lucht.

Met de lichtverstrooingsopstelling zijn deeltjes tot 0.364 μm gedetecteerd, en naar verwachting zullen ook kleinere deeltjes nog waarneembaar zijn. Door met twee detectoren te meten wordt voorkomen dat het pulsvoormige achtergrondsinaal van een fotomultiplicator voor het signaal van een deeltje wordt aangezien. Het is nog niet mogelijk om uit de signalen de grootte van afzonderlijke deeltjes af te leiden. Het intensiteitsprofiel van
De laser zorgt voor spreiding in oppervlak en breedte van de pieken, wanneer deeltjes op verschillende plaatsen de bundel doorkruisen. De verhouding van de piekopervlaktes gemeten met de twee detectoren vertoont deze spreiding niet, maar desondanks is ook deze parameter niet direct bruikbaar. Er bestaat namelijk geen eenduidig verband tussen deze verhouding en de deeltjesdiameter. Het is daarom noodzakelijk om dit gedeelte van het instrument aan te passen. Dit kan bijvoorbeeld middels verkleining van het detectievolume, waardoor een gelijkmatiger belichting ontstaat. Een alternatief is de toepassing van een tweede laserbundel, zodat de aerodynamisch diameter bepaald kan worden door de snelheid van een deeltje te meten.

De gepulste laser wordt met succes aangestuurd door de detectieapparatuur, wat massaspectra van afzonderlijke deeltjes oplevert. In circa 10% van de gevallen wordt een bruikbaar spectrum gemeten. Dit is waarschijnlijk een gevolg van fouten in de uitleijning van de lasers. Het is derhalve nodig om de uitleijningsprocedure te verbeteren. Momenteel kunnen alleen aërosolen met een hoge concentratie gemeten worden, omdat de interne cyclus van de gepulste laser (type Nd:YAG) de meetfrequentie begrenst. Dit probleem zal binnenkort verholpen worden door een ander type laser te gebruiken. Stikstof- en 'excimer'-lasers werken volgens andere principes, waardoor een 2000 maal zo hoge meetfrequentie bereikt kan worden.

De lichtpuls van de verdampingss- en ionisatielaser heeft een intensiteit van circa $3 \times 10^{14}$ W/m². Volgens modelberekeningen is dit vaak voldoende om de vorming van een plasma te veroorzaken. Deze hypothese wordt bevestigd door de gemeten massaspectra, waarin relatief veel ionen met een lage massa voorkomen. In toekomstige experimenten zal een variabele verzwakker worden toegepast, waarmee de intensiteit beter te regelen is. Dit zal waarschijnlijk een gunstig effect op de spectra hebben, met name voor organische verbindingen.

Er zijn massaspectra opgenomen van afzonderlijke deeltjes van een aantal anorganische en organische verbindingen: keukenzout, kaliumchloride, ammoniumsulfaat, een mengsel van de drie voorgenoemde zouten, en ascorbinezuur (vitamine C). De massaresolutie is dusdanig dat pieken met massa 110 en 111 nog onderscheiden kunnen worden, maar dit is niet voldoende om organische stoffen goed te kunnen karakteriseren. Het is aannemelijk dat een aanzienlijk hogere resolutie mogelijk is wanneer alle parameters volledig geoptimaliseerd worden en er een reflecterend veld wordt toegepast. De spreiding in de piekpositie is erg klein voor een set spectra (16 ns op tijdsbasis), zodat dit voor massa's tot circa 600 geen problemen voor de interpretatie oplevert. De spreiding in piekoppervlakte is aanzienlijk (standaarddeviatie 48%), maar de verhoudingen binnen één spectrum lijken representatief voor de samenstelling. Puur ammoniumsulfaat levert goede spectra op, maar in een mengsel met keukenzout en kaliumchloride is deze stof nagenoeg niet aantoonbaar. Op grond van deze waarneming kan worden geconcludeerd dat matrixeffecten belangrijk kunnen zijn.
Dankwoord, Danksagung, Acknowledgements


Wat de experimenten betreft dient allereerst Iwan Satyawan genoemd te worden, die veel werk op het gebied van lichtverstrooiing heeft verzet. Voorts heb ik de laatste 18 maanden samengewerkt met Martin Weiß, die thans het project heeft overgenomen. Martin, mede dankzij jouw inzet is mijn tijd als ‘strohwitwer’ niet verspild geweest. Ik wens je veel succes en ik hoop dat je straks goed kunt opschieten met de bioloog! Ik heb het geluk gehad om bij mijn onderzoek door drie bijzondere mensen te zijn begeleid: Jan Marijnissen met zijn energie, enthousiasme en onbegrensde optimisme, Peter Verheijen, die mij leerde kritisch te zijn op mijn eigen werk en vele ‘wetenschappelijk verantwoorde discussies’ met mij voerde, en Professor Scarlett, die mij vooral veel vrijheid heeft geboden. Tot slot wil ik de leden van de door SON ingestelde gebruikerscommissie hartelijk bedanken voor al hun bijdragen.

Een deel van het werk heeft plaatsgevonden buiten de T.U. Delft. In dit verband wil ik ten eerste de mensen bij het FOM-AMOLF in Amsterdam noemen. Ruud Steenvoorden, Tina Weeding en Piet Kistemaker: we hebben fijn samengewerkt. Bedankt voor de gastvrijheid! Ich bin den Leuten von der Universität Düsseldorf dankbar für ihre Hilfe. Klaus-Peter Hinz, Bernard Spengler und Professor Kaufmann: Vielen Dank. Es war sicher nicht einfach einem Chemischen Technologen das Prinzip eines Flugzeitmassenspektrometers zu erklären! Finally, I want to thank Professor Sheldon Friedlander, his wife Marjory and all students in his lab for making me feel at home during my stay in California.

Ik kan nu terugkijken op ruim vijf jaar binnen de deeltjesgroep en ik ben blij dat ik er al die tijd bij ben geweest. Er heerst altijd een steen van ongedwongen gezelligheid, waaraan de vele conferentiebezoeken en de traditionele vrijdagmiddag-borrels in niet-geringe mate bijdroegen. In dit verband wil ik met name Gabrie en Chiel noemen, die het werken bij deeltjes tot een sociaal gebeuren maakten. Ook andere collega’s hebben hiertoe bijgedragen, zowel in het verleden als in het heden. Gabrie, Peter, Einar, Ron, Johan, Sigrun, Oliver, Lex, Michel, Wim, Ilse, Paul, Marcel, Camiel, Hans, Krijn-Jan, Martin, Silvia, Frank (‘die neue Deutsche Welle’), Alexander, Arief, Damien en alle afstudeerders: bedankt allemaal! Ik hoop dat het ‘deeltjes-gevoel’ nog lang zal blijven bestaan.

Clif
Curriculum vitae