



ON THE PERFORMANCE OF AN ON-LINE TIME-OF-FLIGHT MASS SPECTROMETER FOR AEROSOLS

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Abstract—An instrument has been developed to analyze the size and chemical composition of individual, air-borne particles. The particles are introduced into the vacuum chamber of a time-of-flight mass spectrometer where they are detected and sized using an aerodynamic principle. After sizing, the particles are vaporized by an excimer laser and the resulting ions are analyzed. Experiments have shown that polystyrene particles 1 μm in diameter are not fully vaporized by the laser pulse. The instrument has been characterized and some examples of measurements on ambient and artificial aerosols are presented. Copyright © 1996 Elsevier Science Ltd

1. INTRODUCTION

Single-particle analysis of aerosols remains a topic of current interest in aerosol science (Jambers *et al.*, 1995). Besides size, shape and atomic composition, it is important for some studies to also identify chemical composition of each particle.

In this context, Marijnissen *et al.* (1988) proposed an apparatus for the single-particle analysis of aerosols by combining laser pyrolysis with time-of-flight (TOF) mass spectrometry. The idea is quite simple. Off-line analysis with LAMMA and LIMA (Kaufmann, 1986; van Vaeck *et al.*, 1993) had already demonstrated that TOF mass spectra could be taken from individual, stationary particles, but, amongst other disadvantages, this is a time-consuming procedure because each particle has to be identified manually. The principle is to combine an aerosol beam generator with a TOF mass spectrometer and thus to detect only those particles which pass through the sampling volume of the spectrometer. Several groups (Thomson and Murphy, 1993, 1994; Hinz *et al.*, 1994; Murphy and Thomson, 1995; Prather *et al.*, 1994; McKeown *et al.*, 1991), including our own (Kievit, 1995), have designed such an apparatus and have performed experiments with their own version.

The original paper of 1988 also stressed the possibility of combining these two signals, thus the mass spectrum of each particle with its size, if both can be measured simultaneously. Our design strategy has been to measure size and chemical composition as nearly as possible at the same physical position. The present apparatus does this with not more than 1 mm between the position where the size is determined and where the particle pyrolysis takes place. This produces more accurate and reproducible size measurements than before combined with 100% hit rate sometimes.

This paper describes the development of the complete instrument for both particle size and mass spectrum determination. It focuses on the performance and limitations which are inherent in this method of observation.

2. EXPERIMENTAL SETUP

The aerosol is introduced into the setup by a differentially pumped nozzle/skimmer arrangement. Kievit (1995) reports more details on the design of the aerosol beam generator.

The particle beam is introduced into the ion source of a TOF laser mass spectrometer (Fig. 1). Approximately 2 cm downstream of the last skimmer, the particles travel through the focus of a continuous 16 mW HeNe laser. The particles scatter light which is detected by

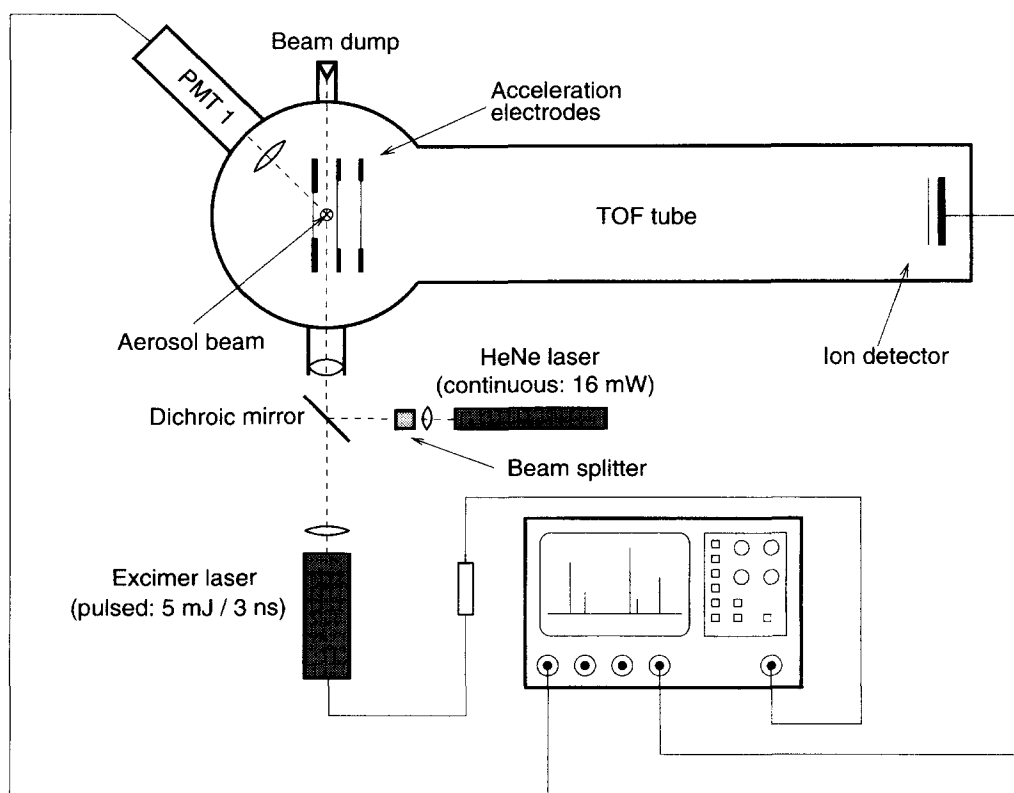


Fig. 1. Schematic top view of the set-up without the beam generator.

a photo-multiplier tube (PMT). The photo-multiplier and the collection lens mounted in front of it are placed in such a way that the light scattered at 45° in the forward direction is collected. This is the smallest possible angle within the present configuration since the mass spectrometer electrodes prohibit a view at smaller angles. The optics collects light from $\pm 20^\circ$ around this angle. A digital oscilloscope (LeCroy model 9354) samples the signal from the PMT at a rate of 500 million readings per second. The oscilloscope also generates a trigger pulse if the PMT signal rises above an adjustable threshold. This pulse triggers an excimer laser which generates ions from the particle. For the experiments a 5 mJ excimer laser with a pulse width of 3 ns was used. The diameter of the focus was estimated to be about $800\ \mu\text{m} \times 400\ \mu\text{m}$ (elliptical shape) resulting in an intensity of approximately $6 \times 10^{12}\ \text{W m}^{-2}$. The laser operates at a wavelength of 308 nm and at a maximum repetition rate of 25 Hz. The total delay time between the detection of a particle and the output of the ionization laser is approximately $1.5\ \mu\text{s}$. The ionization laser is aligned collinearly but displaced downstream of the detection laser by 50–500 μm . This spacing corresponds to the distance traveled by the particles during the delay time.

The ionization process takes place in the ion source of a TOF mass spectrometer. Generated ions are accelerated towards the ion detector, which are multichannel plates, by a two-stage acceleration system. Typical acceleration potentials are of the order of +6 kV. So far, only positive ions have been detected, but the electronic setup can be changed to detect negative ions instead. The signal of the ion detector is digitized by the oscilloscope simultaneously with the photo-multiplier signal and both are sent, after acquisition, to a PC via a GPIB bus interface. After receiving the data the PC rearms the system for the next trigger and acquisition. Data processing is carried out on a UNIX-based workstation connected to the PC in an Ethernet-based network.

In this way the instrument offers information on the size (PMT signal) and the chemical composition (mass spectrum) of single particles. No sample preparation is necessary, so the instrument can be operated on-line. The maximum repetition rate is about 2–10 Hz

depending on the necessary mass range of the mass spectrometer and the resulting amount of data, because the data transfer between the sampling oscilloscope and the computer is the limiting factor.

3. PARTICLE DETECTION AND SIZING

The signal of the PMT serves two purposes. Firstly, it is used to trigger the excimer laser that vaporizes the particle. Secondly, the PMT signal can be used to gain information on the size of the particles. This section of the paper explains how the size information is obtained in the Delft on-line aerosol analysis system.

Kievit (1995) investigated the analysis of PMT signals, considering the width of the peaks and ratios of signals obtained from different angles. He failed however, to obtain reliable size information because of the inhomogeneous laser intensity profile. Special diffraction optics can be used to obtain a more “top hat” profile from the laser (Murphy and Thomson, 1995; Thomson *et al.*, 1994; O’Shea, 1985). Since this optics reduce the overall intensity considerably, strong and therefore expensive lasers must be used to achieve reasonable detection limits. Thomson and Murphy (1994) used, for example, a 80 mW, diode-pumped, frequency-doubled Nd–YAG laser. For the work described here a different approach was implemented that is explained in the next section.

3.1. Aerodynamic particle sizing

It is well known (Dahneke and Friedlander, 1970; Dahneke and Padliya, 1977; Dahneke, 1978) that the velocity of the particles is size dependent after passing a beam generator assembly such as the one described above. Commercial aerosol spectrometers are available which use this effect for rapid, on-line particle-size distribution monitoring (Baron, 1986; Willeke and Baron, 1993).

In the beam generator, the aerosol stream is expanded and accelerated through a nozzle. Because the pressure ratio across the nozzle is smaller than 0.5 the air reaches supersonic velocity. Since the particles have higher inertia than the gas molecules they cannot fully follow the acceleration and thus attain a size-dependent terminal velocity. The speed of the particles is determined by measuring the transit time of the particle between two laser beams.

Recently, Prather *et al.* (1994) implemented such a sizing system into an on-line TOF mass spectrometer for aerosols. To implement this sizing technique in the Delft system the incident HeNe laser beam was split so that two focal points are obtained in the vacuum chamber (Fig. 2). Splitting the laser beam reduces the intensity of each focal point by more than 50% in comparison with the single beam but the alignment is easier with this arrangement than one using a second laser as Prather *et al.* (1994) did. Furthermore, the spacing between the two lasers is smaller which increases the hit rate and reduces coincidence errors (see below). The spacing is fixed for a given prism and therefore easy to reproduce.

For the experiments a Melles Griot Inc. beam displacing prism model 03 PPD 301/A was used to split the laser beam. This prism provides a displacement of 2.6 mm at 632.8 nm, is coated with an anti-reflex coating for 632.8 nm, and is of low scatter grade. The transmission efficiency of the prism is 84%, i.e. 42% per exiting beam. Figure 3 shows the resulting photo-multiplier signal for a 1 μm polystyrene latex (PSL) particle. The triggering system was designed to trigger at the occurrence of the *second* peak in the signal to avoid a vaporization of the particle by the ionization laser before its sizing is completed. This second peak must follow the first within a specific time interval in order to cause a trigger. The time between the two first peaks (7.8 μs in Fig. 3) is a direct measurement of the velocity of the particles.

From Fig. 2 another advantage of this configuration becomes obvious. Particles with trajectories that are not exactly vertical (i.e., are off-axis) do not pass *both* detection foci. Therefore, the trigger system does not detect a second peak inside the timing window and

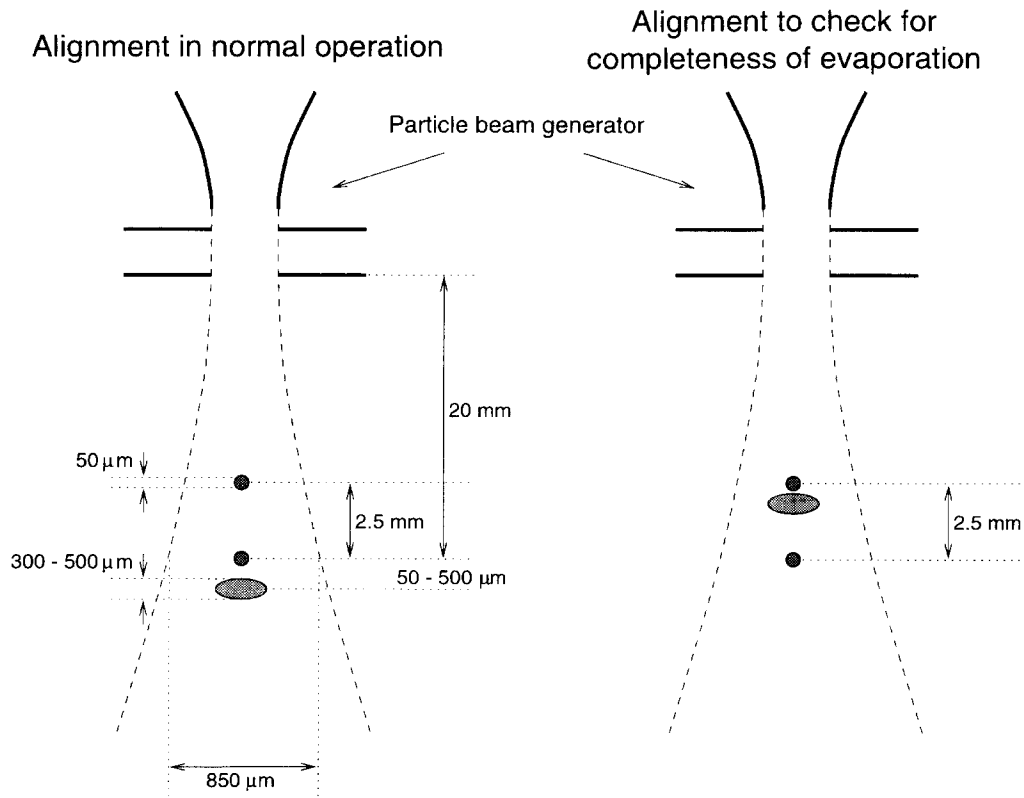


Fig. 2. Side view of the laser alignment with implemented beam splitter.

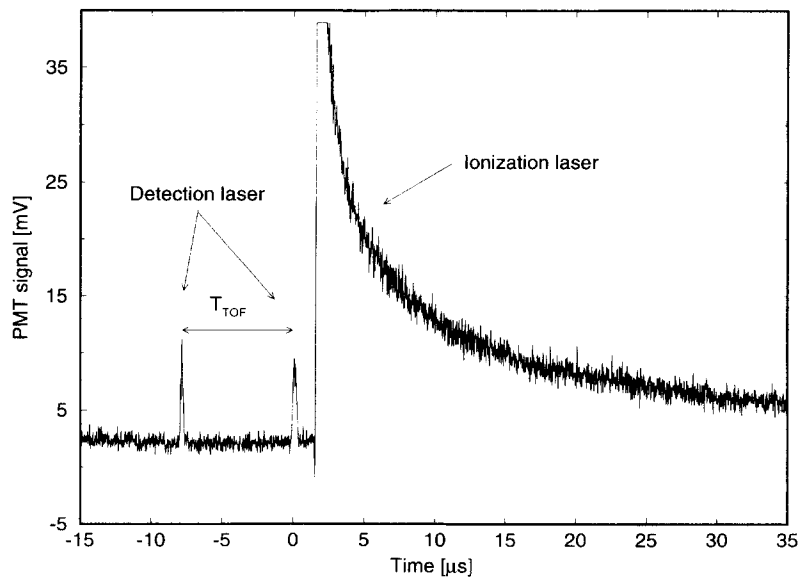


Fig. 3. PMT signal of a 1 μm latex particle with implemented beam splitter.

does not trigger the ionization laser. This leads to an effective horizontal extent of the ionization zone that is much smaller than the diameter of the focus of the ionization laser. Shot-to-shot variations in the TOF of the ions are therefore reduced which improves the accuracy of the calibration of the mass spectrometer.

In order to obtain a calibration curve measurements were made with several sizes of latex particles which were obtained from Duke Scientific Corp., Palo Alto, California. Figure 4

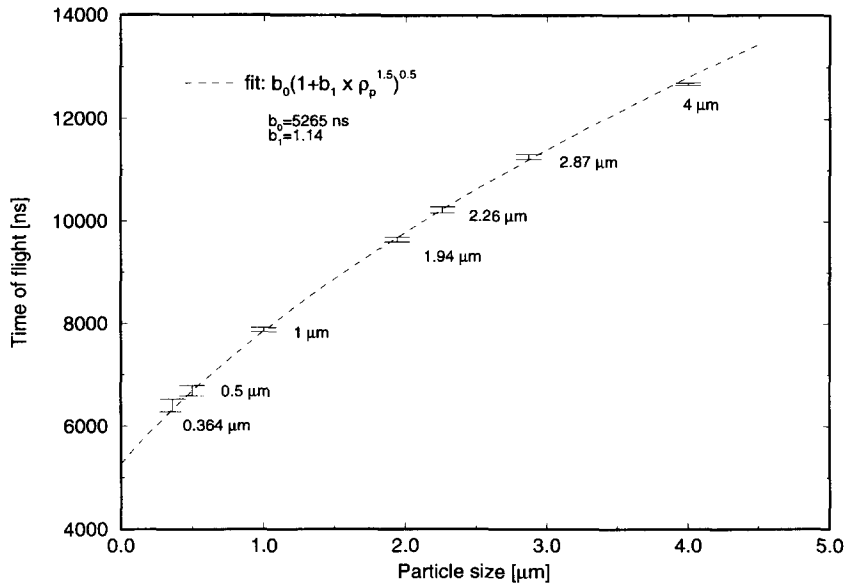


Fig. 4. Calibration curve for aerodynamic particle sizing.

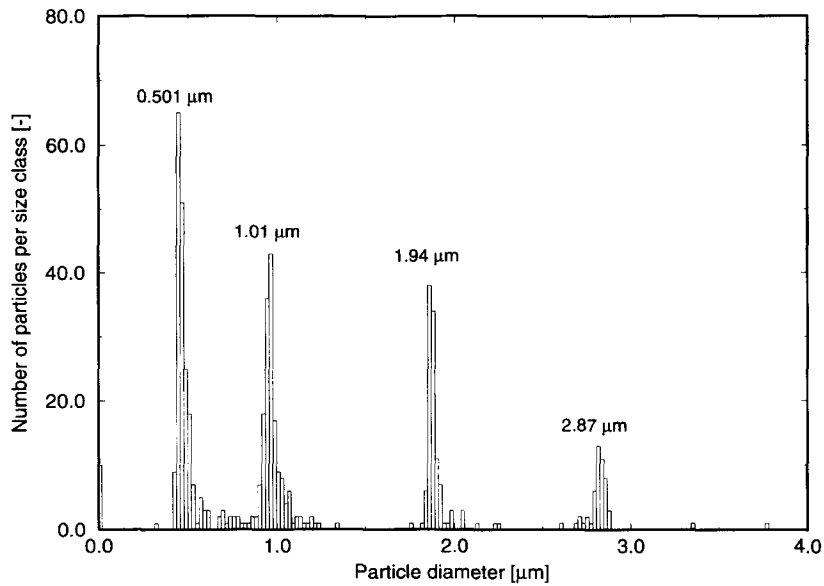


Fig. 5. Size measurement of 4 fractions of latex (each with a uniformity better than 5%).

shows the resulting calibration curve. Sub-micrometer particles as small as $0.5 \mu\text{m}$ can be measured with very small error. Each point on the calibration curve represents the median of several hundred particles. This calibration curve is only valid for spherical particles of the same density as polystyrene latex. During the acceleration through the nozzle Stokes law is not applicable because of the high particle Reynolds numbers. The resulting terminal velocity is therefore not a unique function of the aerodynamic diameter (Willeke and Baron, 1993).

Figure 5 shows an example of a measurement of an aerosol consisting of a mixture of four latex fractions. The four sizes are easily resolved by the aerodynamic sizing system.

An important source of error in TOF aerosol spectrometers is coincidence of the particles (Heitbrink *et al.*, 1991). When a particle enters the sensing zone while another one is already present, a wrong measurement results. The probability of this error is a function of the rate

of detected particles, λ , and the residence time of the particles in the sensing zone, T . Using Poisson statistics the coincidence error $e(\lambda, T)$ can be estimated by the following expression:

$$e(\lambda, T) = \sum_{n=1}^{\infty} \frac{(\lambda T)^n}{n!} e^{-\lambda T} = 1 - e^{-\lambda T}. \quad (1)$$

The 10% coincidence mark is reached at detection rates above 10,000 particles per second, assuming a typical TOF of 10 μ s. Such high detection rates were observed when an ultrasonic nebulizer was used to generate aerosols from solution (estimated number concentration 10^7 cm^{-3}). To overcome this problem either the incoming aerosol must be diluted or the distance between the two detection foci, and consequently the TOF, must be reduced. A successful and reproducible reduction of this spacing was facilitated by using a diffraction grating as a beam splitter in place of the beam displacing prism. Typical spacings using a grating with 10 lines per mm are of the order of 250 μ m. The residence times of the particles in the sensing volume decreases by a factor 10 and thus the tolerable count rate increases by a factor 10.

4. CHARACTERIZATION OF THE AEROSOL BEAM

Two parameters of the aerosol beam were determined, i.e. the width of the particle beam at the point of detection and the velocity of the accelerated particles.

4.1. Width of the particle beam

The particle beam diameter was measured by scanning the detection laser beam, before splitting, horizontally through the particle beam with an adjustable translation table. The rate of detection of the particles (1 μ m polystyrene latex) was measured as function of the laser position (Fig. 6).

In order to relate this displacement to that of the beam in the vacuum chamber the system was opened and a photo sensitive paper mounted at the focal plane. The scan was now

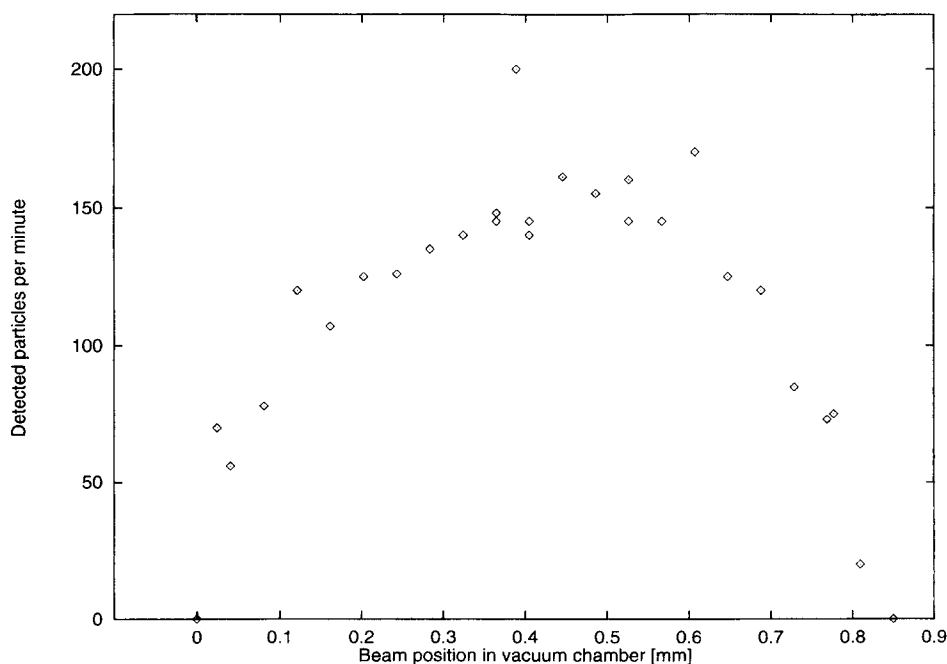


Fig. 6. Concentration profile in the particle beam.

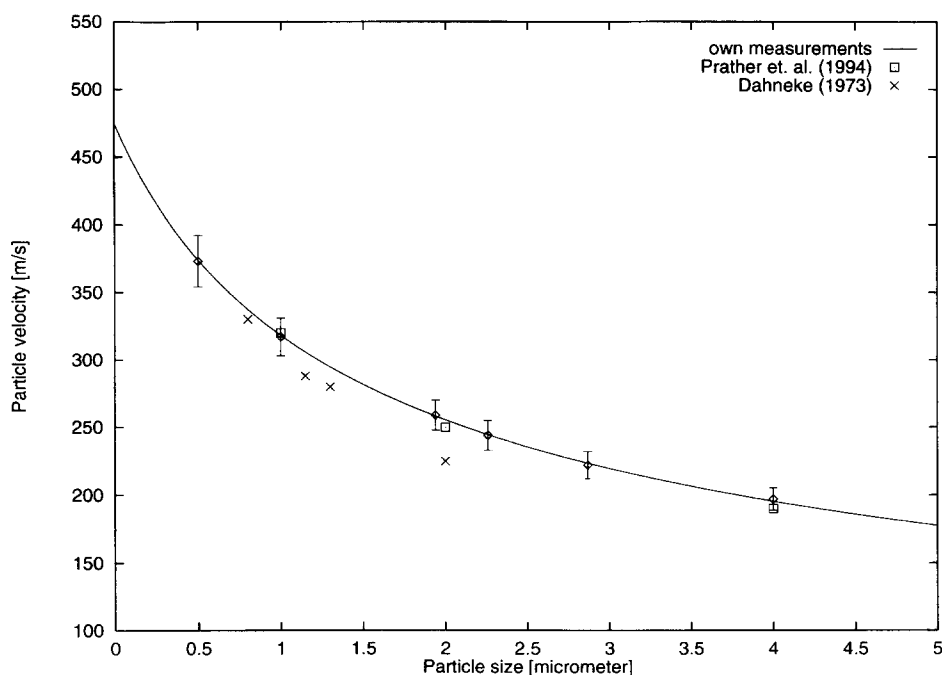


Fig. 7. Particle speed as function of particle size.

repeated over the previously measured range leaving a trail on the photo paper. The length of the trail was then measured by a calibrated microscope. The trail proved to be $850\ \mu\text{m}$ long which consequently is the diameter of the particle beam at the height of the detection zone. Since the diameter of the detection laser focus is only about $50\ \mu\text{m}$, it is clear that most of the particles exiting the beam generator remain undetected.

4.2. Velocity of the particles

Because the relationship between the TOF and the particle size is already known (Fig. 4), the velocity can be related to the particle size by measuring the distance between the foci. This was done by using an adjustable translation table equipped with a knife edge which was mounted above the electrodes of the mass spectrometer.

Using the polarizing beam splitter the distance between the focus points was measured as $2.5 \pm 0.1\ \text{mm}$. This coincides to a beam displacement of the prism of $2.6\ \text{mm}$ at $632.8\ \text{nm}$ and a lateral magnification of 0.95 by the imaging lens. Using this information the calibration shown in Fig. 7 is obtained. The error in this curve is mainly due to the inaccuracy of the laser spacing measurement. The velocity measurements agree remarkably well with the ones made by Prather *et al.* (1994) although these were made with NaCl particles. Dahneke (1973) measured slightly lower velocities. This is probably due to the different nozzle geometries and pressures.

5. MASS SPECTROMETRY OF AEROSOL PARTICLES

5.1. Influence of the laser energy on the appearance of the mass spectra

The intensity and wave length of the ionization laser are important parameters for the mass spectra. The ionization laser produces $5\ \text{mJ}$ of light at a wavelength $308\ \text{nm}$ within $3\ \text{ns}$. To investigate the influence of the ionization laser energy on the mass spectra the laser beam was attenuated using glass slides. Since these glass slides are made of conventional glass they absorb significant amounts of UV radiation. Using several of these slides in series results in an attenuation of the laser beam. The energy output of the laser after attenuation was checked periodically during the experiments with a pyroelectric energy detector.

The influence of the laser energy on the mass spectra of 1 μm polystyrene latex particles is shown in Fig. 8. Similar spectra have been reported by Hinz *et al.* (1994). The spectra show typical clusters of one, two or more carbon atoms. The effect of the high energy can clearly be seen. The incidence of small fragments tends to increase with higher energy.

The influence of the energy is even more marked in the case of anthracene particles as can be seen in Fig. 9. Below a certain threshold the polycyclic anthracene molecule (molecular

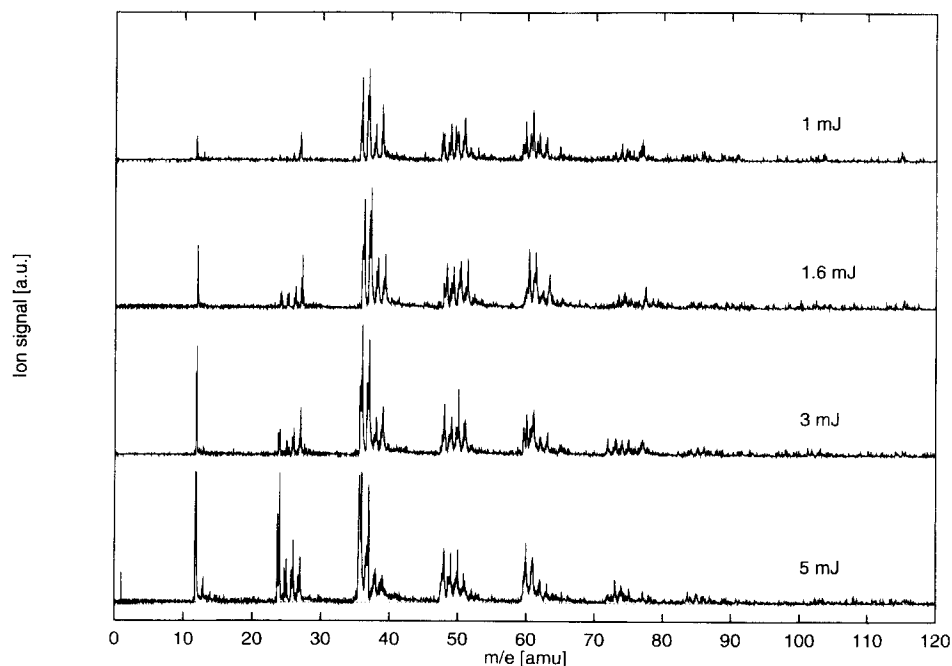


Fig. 8. Energy influence on spectra of polystyrene latex particles.

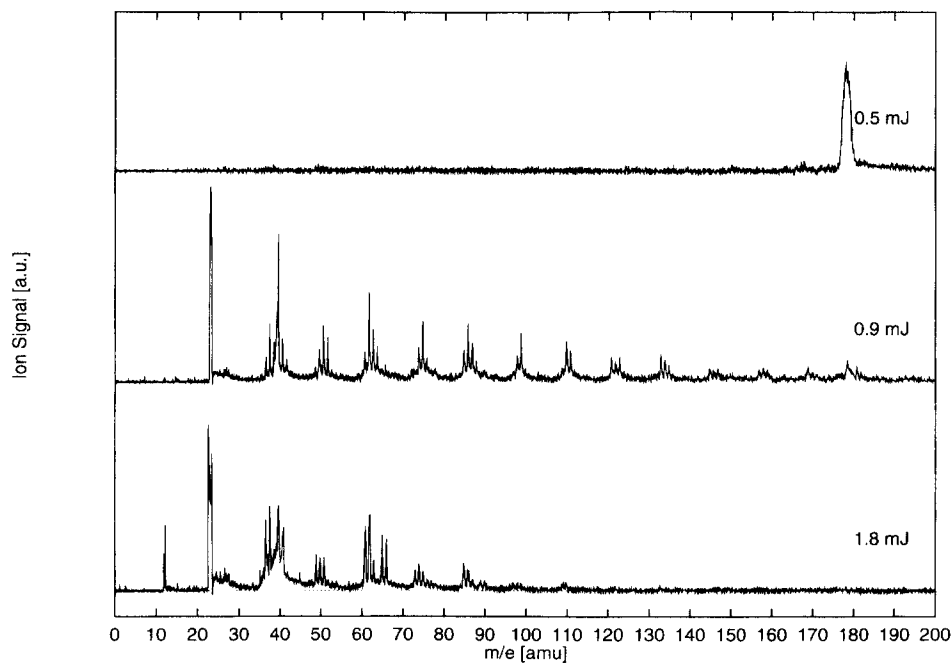


Fig. 9. Energy influence on spectra of anthracene particles.

mass 178 amu) stays intact and only the single peak of the molecular ion can be seen. For higher energies the molecule breaks down to carbon clusters.

5.2. Hit rate

An important performance parameter for on-line single particle mass spectrometry systems is the hit rate. Once a particle is detected by the photo-multiplier the ionization laser is triggered. The timing and alignment of this laser must be matched with the particle velocity in order to hit the particle. The excimer laser which was used introduces, together with the triggering electronics, a delay time of approximately $1.5\ \mu\text{s}$ between the external trigger input and the radiation output with a variation of only a few nanoseconds. The width of the operating window can be calculated using the knowledge of the diameter of the focus, laser delay time and particle velocity as function of particle size.

Obviously, a hit rate of 100% should be attainable for mono-disperse particles assuming a correct alignment and that all the particles have the same velocity. This was confirmed by experiments using mono-disperse latex particles. For the polydisperse case however only a certain size fraction will be hit by the laser. Small particles which travel faster are too far downstream at the moment of firing and the large particles are not far enough.

In order to prove this the following experiment was carried out: an aqueous solution of sodium chloride (0.33 wt%) was nebulized using a DeVilbiss Model 40 pneumatic nebulizer. The spray was heated and dried in a diffusion drier resulting in an air stream containing polydisperse sodium chloride crystals. The aerodynamic mean diameter was $0.88\ \mu\text{m}$ with a geometric standard deviation 1.33 as measured with an API Aerosizer. The aerodynamic sizing system was used to measure the particle-size distribution entering the vacuum chamber. Simultaneously, it was noted from which particles spectra were obtained. The result obtained with the default alignment (Fig. 10) clearly shows the operating window. When the spacing between the detection and ionization laser was enlarged the system becomes sensitive to the smaller, faster particles, as expected and as shown in Fig. 11.

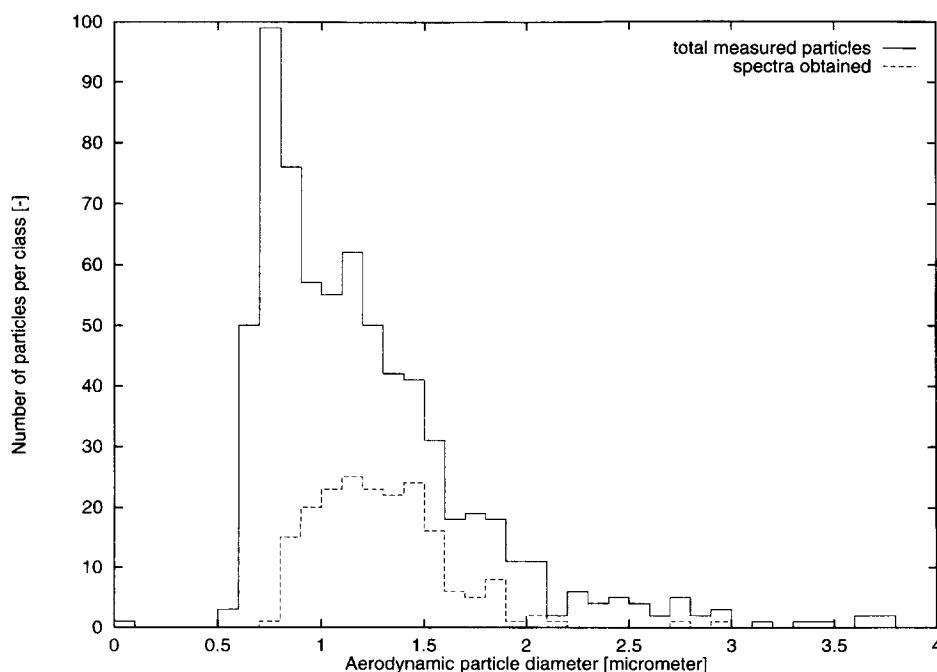


Fig. 10. Hitting performance for NaCl particles with default alignment (laser energy 1.9 mJ).

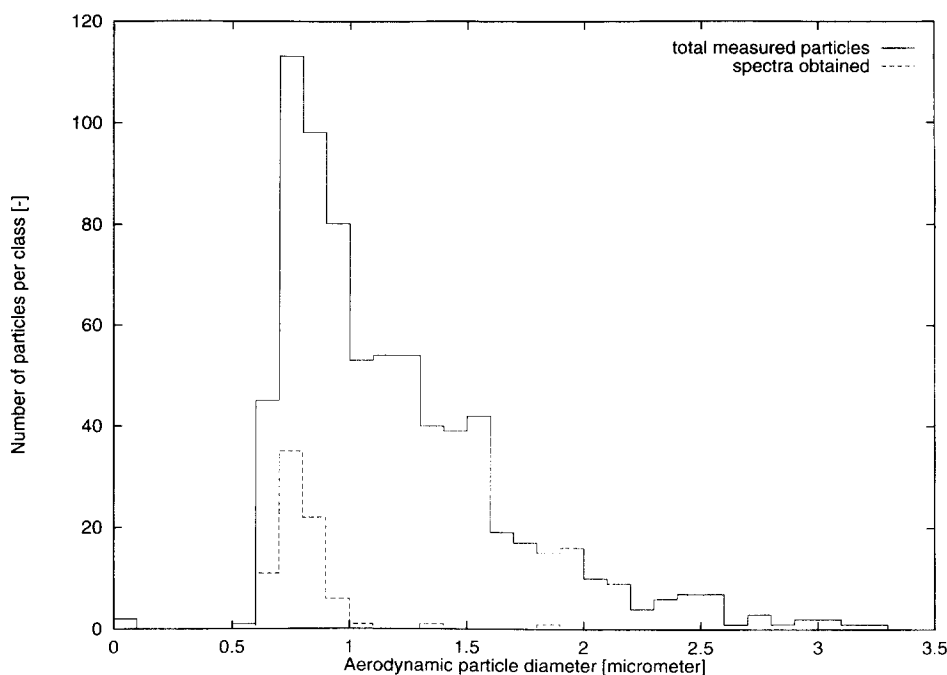


Fig. 11. Hitting performance for NaCl particles with alternative alignment (laser energy 1.9 mJ).

In order to enlarge the width of the operating window several approaches are possible:

1. Use of higher laser power will lead to a larger usable focus diameter and, therefore, to a wider operating window but will also increase fragmentation of fragile molecules.
2. Shorter laser delay times minimize the spatial spread of the particles and, therefore, enlarge the operating window.
3. Active triggering, as reported by Prather *et al.* (1994), uses the information already obtained to delay the trigger depending on the particle speed. This requires however bigger distances (about a factor 100) between the laser foci which results in reduced hit rates and higher probability of coincidence errors (see above).
4. Scanning of the laser beam or laser delay time as reported by Hinz *et al.* (1994) allows the measurement of broad size distributions but increases the time to obtain a representative measurement.

5.3. Completeness of evaporation

For many applications it is useful to know whether or not the particles are completely vaporized by the ionization laser. If the particles are not completely vaporized, the recorded mass spectrum is not necessarily representative of the *whole* particle. This is important in the case of inhomogeneous particles which may consist of different core and shell materials. In order to investigate whether parts of the particle survive, a post detection laser was installed after the ionization as shown in the right part of Fig. 2.

The electronics was adapted for this experiment to trigger on the first peak. Two cases are possible. If the particles are completely evaporated, nothing should be seen on the photomultiplier after ionization takes place. If, however, the particle partly survives, a second peak should be seen *after* ionization. The experiments were carried out with a monodisperse latex aerosol at very low concentration (less than 1 count per second) in order to avoid coincidence errors. Figure 12 shows a typical result when a 1 μm particle was analyzed using a medium laser energy.

A second peak can clearly be seen after ionization which indicates that the particle was not completely vaporized. The simultaneously acquired mass spectrum ensures that the

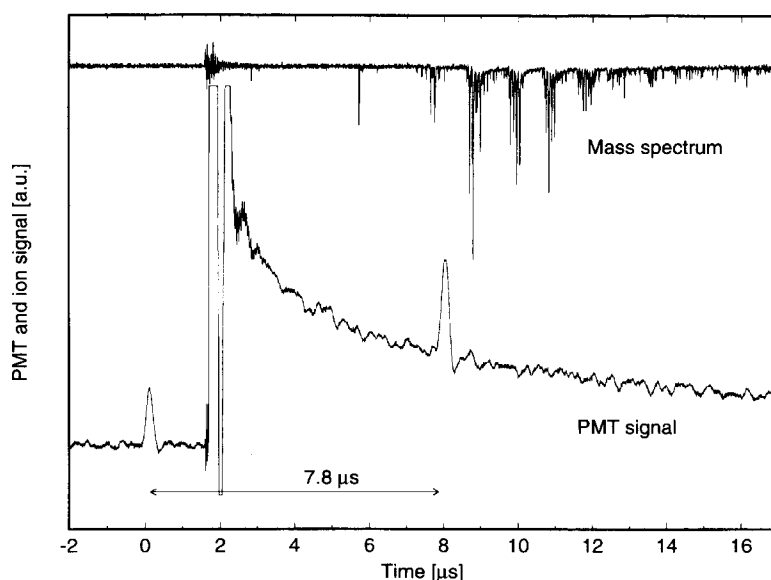


Fig. 12. Test for complete evaporation of a $1\ \mu\text{m}$ PSL particle (2.9 mJ).

particle was in fact hit by the ionization laser and that it was a latex particle. The time between the two peaks resulting from the scattering of the HeNe laser was approximately $7.8\ \mu\text{s}$ which is exactly the time from the calibration curve (Fig. 4) for a $1\ \mu\text{m}$ particle. This means that the particle did not change its speed during the analysis.

The same experiment carried out with maximum laser energy (5 mJ) results in practically the same signals.

This experiment shows that latex particles of the order of $1\ \mu\text{m}$ are *not* completely vaporized by the laser. The degree of vaporization can, however, not be determined by that experiment. It can only be concluded that the surviving particles are greater than $0.4\ \mu\text{m}$ since this is the detection limit of the sizing system.

5.4. Mass spectra of various particles

In this section some spectra of ambient and artificial aerosols are presented. Figure 13 shows two spectra of NaCl particles. The aerosol was produced by nebulizing a sodium chloride solution (0.33 wt%). This solution was made with distilled water in the case of the upper spectrum and with tap water in the case of the lower spectrum. Peaks for sodium (23 amu), Na_2Cl (81/83 amu) and Na_3Cl_2 (139/141 amu) are present in both spectra. The additional peaks in the lower spectrum can be related to the impurities of the tap water. Potassium (39 amu), calcium (40 amu), CaO (56 amu) and CaCl (75/77 amu) can be identified.

Figure 14 shows two typical spectra obtained from an analysis of ambient air in the laboratory. The upper spectrum is the one most often observed during the experiment. The high sodium (23 amu) and potassium (39 amu) peaks indicate a salt particle. The experiments were carried out in Delft, The Netherlands, which is located close to the North Sea (about 20 km). The particle is, therefore, likely to be of maritime origin. A closer look at this spectrum shows that the particle also contains significant amounts of calcium (Ca (40 amu), CaO/CaOH (56/57 amu)).

The second particle (lower part of Fig. 14) is characterized by low sodium and potassium content and a high abundance of calcium. The particle most likely originates from building materials containing CaSO_4 .

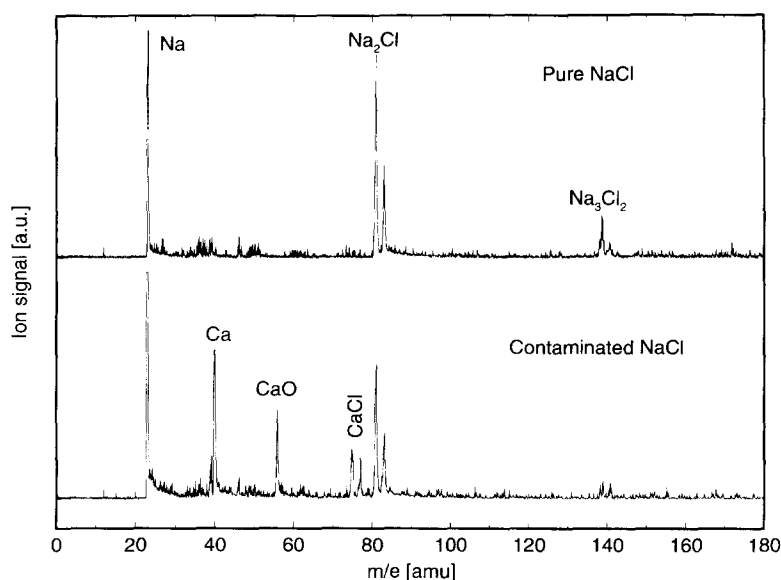


Fig. 13. Two spectra of sodium chloride.

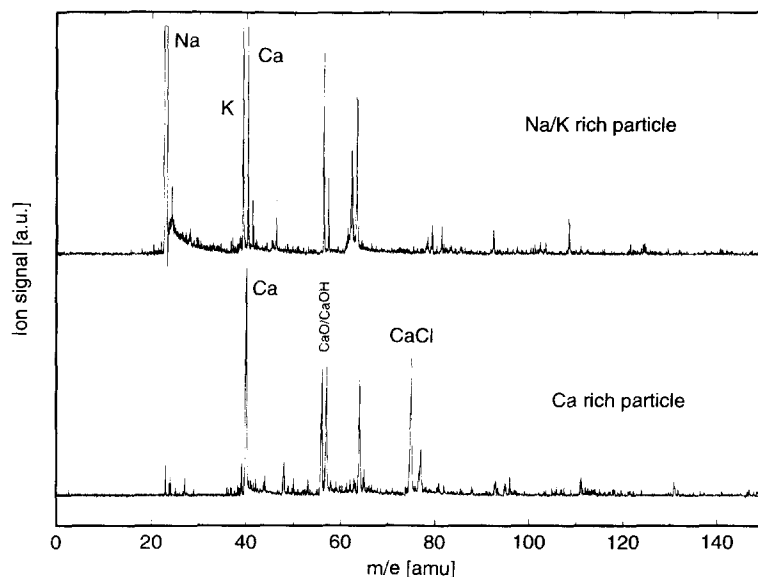


Fig. 14. Two spectra from particles of ambient air.

6. CONCLUSIONS AND DISCUSSION

With the TOF mass spectrometry system described here single aerosol particles can be analyzed on-line by means of laser desorption/ionization mass spectrometry. The size of the individual particles can be measured simultaneously. The sizing system is based on an aerodynamic principle. Particles in the size range from 0.4 to 10 μm have been analyzed with this system. The particle velocities measured are in good agreement with literature values. Since the width of the particle beam at the detection point is around 850 μm only a small fraction of the particles entering, is detected. Thus, if aerosols are to be measured at low concentrations the time to obtain a representative sample must be increased.

Because of the fixed timing of the triggering electronics and the spread in particle velocities only a certain size fraction can be analyzed at one time. The width of this

operating window is different for different materials. In order to measure wide size distributions, say from 0.5 to 5 μm , either the laser or the delay time must be scanned.

The 5 mJ excimer laser does not vaporize 1 μm latex particles completely. If particles are not homogeneous the information in the mass spectrum may therefore not be representative of the whole particle. On the other hand, this also means that the system can be sensitive to surface contamination on the particle.

Organic and inorganic particles of various substances have been successfully analyzed. During the experiments a significant variation in the mass spectra became apparent even if mono-disperse and chemically homogeneous particles were analyzed. The amount of variation appears to be dependent on the materials analyzed and the ionization laser energy used. Work is in progress to quantify this effect.

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