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THE ON-LINE CHEMICAL ANALYSIS OF SINGLE PARTICLES USING AEROSOL BEAMS AND TIME OF FLIGHT MASS SPECTROMETRY

O. KIEVIT, M. WEISS, P. J. T. VERHEIJEN, J. C. M. MARIJNISSEN* and B. SCARLETT

Delft University of Technology, Faculty of Chemical Technology and Materials Science, Particle Technology Group, Julianalaan 136, 2628 BL Delft, The Netherlands

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This paper describes 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 is that a working 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.

KEYWORDS Chemical analysis Photo-ionization Aerosol beam Time-of-flight mass spectrometry

INTRODUCTION

It is well-known that airborne particles (aerosols) affect human health and the environment, and that they can damage electronic equipment. Next to size and concentration, the chemical composition of a particle is an important parameter. Sheldon Friedlander already noted this in 1977, when he published his famous book 'Smoke, dust and haze' (Friedlander, 1977). Unfortunately, the standard techniques for the chemical analysis of an aerosol measure the average composition of the particles, which are usually collected on a filter or impactor. There is a limited number of techniques available for the chemical analysis of single particles, of which laser microprobe mass spectrometry (LAMMA) and particle-induced X-ray emission (PIXE) are most widely used. It is however always necessary to collect the particles first, which can introduce size selectivity, as well as artifacts due to the time delay and sampling preparation. Some of these errors can be avoided by employing aerosol beam techniques. An aerosol or particle beam forms when an aerosol is expanded through a small orifice into a vacuum chamber, as illustrated by Figure 1. The difference in

^{*} Author to whom correspondence should be sent.



FIGURE 1 Operating principle of an aerosol beam generator.

inertia between the particles and the gas molecules causes the actual formation of the beam. Once captured in the beam, it is easy to transfer a particle to an analysis section, where its size and chemical composition can be measured.

Particle size 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. This technique can conveniently be applied to an aerosol beam, also enabling a subsequent chemical analysis. In a similar way, the interaction of an electric field with a charged particle can be used to measure particle size. However, in this case it is not easy to combine the size measurement with an aerosol beam. The time-of-flight aerodynamic particle spectrometry is the most widely applied of the combined physical techniques. The operation of a time-of-flight aerodynamic particle sizer (not to be confused with a time-offlight 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 using two laser beams, which is related to its aerodynamic diameter. This technique was first combined with the chemical analysis of single particles by Sinha and coworkers (Sinha, 1984).

At present there are only two methods described in literature 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.

CHEMICAL ANALYSIS OF SINGLE PARTICLES

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; Giggi et al., 1989). In the early versions of the instrument the particles impinge directly upon a resistively heated metal filament where the aerosol material is ionized by surface ionization. The ionization efficiency is highly dependent on the analyte ionization potential and only materials with low potentials (< 8 eV) can 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 photo-ionization, as was first suggested by Dahneke (1980).

Sinha (1984) was the first to use photo-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 located at 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:

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

A possible disadvantage of this vaporization/ionization method is that it is very complex, and not yet fully understood.

Some years later Marijnissen *et al.* (1988) published a paper proposing improvements on the technique (see Fig. 2). These improvements include the usage of a single He-Ne laser beam for the sizing and detection of the particles and for the triggering of the chemical analysis cycle. Furthermore the application of a pulsed UV laser is suggested, to enhance ionization.

Conclusively the application of a time-of-flight mass spectrometer is suggested, which, unlike quadrupole or focal plane types, produces a complete mass spectrum from one single burst of ions. The development of an on-line chemical analysis technique for single aerosol particles is currently the subject of several research projects (McKeown *et al.*, 1991; Hinz *et al.*, 1994; Prather *et al.*, 1994). This paper reports some of the most important results obtained at the Delft University of Technology (Kievit, 1995). The setup is largely based on the suggestions from Marijnissen *et al.* (1988), but vaporization and ionization are achieved by one single laser pulse.



FIGURE 2 Outline of the apparatus proposed by Marijnissen et al. (1988).

THE AEROSOL BEAM GENERATOR

Introduction

Aerosol beams have been studied since 1964 (Murphy and Sears). Important contributions on 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). This chapter will describe the characteristics of an aerosol beam generator which is optimized for the given application. It has been designed using computational fluid dynamics (CFD), theoretical models, earlier results (Kievit, 1990) and work from other authors. Since the application of a time-of-flight mass spectrometer is intended, it is necessary to create a vacuum of at least 10^{-4} Pa at the analysis section. As one stage can achieve a pressure reduction of roughly a factor 1000, this implies that three pumping stages are required. The sample flow rate is determined by the cross section of the first orifice (the nozzle), provided the ratio of the pressures upstream and downstream from the nozzle exceeds a critical threshold:

$$\frac{p_b}{p_0} = 0.5283$$

In this case the gas reaches sonic velocity in the nozzle exit, which restricts the flow rate. Downstream from the nozzle the velocity increases further, reaching supersonic values. Both calculations and experiments show that with a nozzle diameter of 0.3 mm the flow rate is approximately 0.9 l/min.

Shock Waves

As in every supersonic expansion, shock waves can occur 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 will disturb the gas flow and prevent the generator from working optimally, especially for the lower particle size range. It is therefore necessary to design the aerosol beam generator in such a way that the formation of shock waves is minimized. The location of the second and third limiting orifices (skimmers) can 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 skimmer 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 Fig. 3). Instead, the skimmer will behave 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 will be low, and therefore the disturbing effects usually caused by a Mach disk will be reduced significantly.

Bier and Schmidt also found that for a fixed value of γ , the shape and size of the barrel shock are solely determined by the pressure ratio across the nozzle. Although not noted by the authors, their experiments show that all of the characteristic lengths of the barrel shock, as defined in Figure 3, can be described by a single relation of the form

$$\frac{L_{\rm c}}{D} = C_1 \left(\frac{p_0}{p_b}\right)^{C_2} \tag{2}$$

which enables the determination of size and location of the barrel shock within 5%. Table I lists the values of the two constants in Equation 2 for each of the characteristic dimensions specified in Figure 3, in the case of a diatomic gas ($\gamma = 7/5$). These values were obtained by fitting the experimental data 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 and found slightly different values for 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. The distance at which the diameter of the Mach cone is maximal (x_R) can be calculated with this equation.



FIGURE 3 Characteristic lengths of the barrel shock.

TABLE I

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

Characteristic length L_c	Empiric C1	cal constants C_2
x _R	0.47	0.49
X _M	0.74	0.49
X _R	0.89	0.49
Y _B	0.38	0.56
Ум	0.31	0.56
y_R	0.45	0.56

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. It is possible to shift the Mach cone beyond the second skimmer as well by employing the same criterion. The distance at which the second skimmer has to be placed will depend 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, a distance smaller than 5.5 mm should be used; the present setup uses 5 mm.

Efficiency

Ideally, the instrument should analyze every particle that enters. The transport efficiency of the aerosol beam generator must therefore be high, but in general this will not be the case for the entire size range. Two different nozzle geometries, shown in Figure 4, were modelled with the Computational Fluid Dynamics package Fluent^{\circ}, to investigate the influence of particle size on the transport efficiency. Nozzle A can be manufactured by drawing a glass tube into a capillary, thus creating a smoothly converging flow channel. In principal, the range in which the nozzle diameter can be chosen is unlimited. Nozzle B can be manufactured from metal, using standard machining techniques. The orifice is created by spark discharge machining, a technique which is frequently used to make holes down to 0.1 mm in diameter. In the modelling study the inlet and outlet pressures were fixed, and the compressibility of the fluid was taken into account. The standard program was extended with a user- defined subroutine to calculate the drag force at various flow conditions. The drag force can be written as

$$F_{D} = \frac{\pi d_{p}^{2}}{4} \frac{\rho u_{rel}^{2} C_{D}}{2 C_{C}}$$
(3)



FIGURE 4 Geometrical outline of the nozzles A and B, modelled with Fluent^e. The exit diameter is 0.5 mm in both cases.

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 which are small as compared to the mean free path of the gas molecules, which is a function of temperature and pressure. In the modelling study the particle diameter has been varied from $0.02 \,\mu\text{m}$ to $20 \,\mu\text{m}$, the usual range of interest in aerosol technology.

By varying the size of the particles injected in nozzle B, three trajectory regimes can be distinguished (Fig. 5). Small particles ($d_n \le 0.8 \,\mu\text{m}$) are able to follow the streamlines and leave the nozzle with trajectories that 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 ($d_p > 0.8 \,\mu\text{m}$) 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. If the same particle size range $(0.02-20 \,\mu\text{m})$ 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 wall around the skimmer, which makes nozzle A more suitable for transporting relatively large particles. The results are summarized in Figure 6, which shows the percentage of particles in each of the three regimes, for particle sizes ranging from 0.02 to 20 μ 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). It can be concluded that in both cases the transport efficiency depends on particle size. Nozzle A has the highest transport efficiency if the particles are $2 \mu m$ or bigger; nozzle B is the better choice if particles smaller than $2 \mu m$ are to be analyzed.

Size selectivity can, for example, 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. Alternative methods to increase the transmission efficiency for a specific particle size have been described by Rao *et al.* (1993) and Liu *et al.* (1993). The effect of the magnitude of the sheath air flow on the transport efficiency of nozzle B is shown in Figure 7. The region with 100% efficiency can be extended from $0.8-1.0 \,\mu\text{m}$ to $0.5-2.0 \,\mu\text{m}$, 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 will be reduced to approximately 16% of the original value. It is therefore not advisable to apply sheath air when the particle concentration is low.

Experimental Setup

Figure 8 shows the experimental aerosol beam generator, built as an inlet for the instrument. A sample is drawn into a 20 cm length, 1 cm inner diameter stainless steel



FIGURE 5 Overview of the three trajectory regimes found in the modelling study: a: $d_p \le 0.8 \,\mu\text{m}$, b: $d_p > 0.8 \,\mu\text{m}$, c: $d_p > 2.0 \,\mu\text{m}$.



FIGURE 5 (Continued).

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 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 (pressure approx. 1 mbar), which is pumped by a $12 \text{ m}^3/\text{hr}$ 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) and the pressure is in the order of 10^{-2} mbar. 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 CR63/150 M). At this point the pressure has been reduced to 3×10^{-6} mbar, which is sufficiently low to operate the mass spectrometer.

OPTICAL DETECTION AND SIZING

Optical Setup

A 16 mW multimode helium-neon laser (Melles Griot model 05-LHR-981) is used for the detection and sizing of the particles. A two-lens system focuses the laser beam in the



FIGURE 6 Percentage of particles in each of the three trajectory regimes for nozzle A (top) and B (bottom).

centre of the analysis section, where it crosses the aerosol beam. Two photomultiplier tubes mounted at 45 and 90° (Thorn-EMI model 9202B) collect the light scattered by every particle as it passes the laser beam. By using two detectors instead of one, false triggers caused by dark spikes are avoided. The scattering signals are recorded by digital oscilloscope and transferred to a personal computer for processing.



FIGURE 7 Influence of the amount of sheath air on the transport efficiency of nozzle B.

Results

Particles from 0.364 to 8.0 μ m in diameter have been detected with the experimental setup, using nozzle geometry A. The small particles are monodisperse polystyrene latex spheres ($\leq 3 \mu$ m), dispersed by nebulizing commercially available suspensions. The large particles are corn oil droplets (> 1 μ m), produced using a vibrating orifice aerosol generator (TSI model 3450). The efficiency at which particles are detected is size dependent, and it ranges from 2% for 2 μ m particles to 40% for 8 μ m particles. This is not just the result of a lower transport efficiency; small particles are more difficult to detect as they produce signals with a lower amplitude. The signal amplitudes measured for a monodisperse aerosol display are not very constant, as is illustrated by Figure 9. The large variation in amplitude is caused by what is generally called the intensity ambiguity problem. The spatial intensity distribution of the laser focus is not uniform, which results in different signal amplitudes and width for identical particles passing through different parts of the beam.

Area Ratio

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. In the case of a monodisperse 4 µm corn oil aerosol, the distribution of the signal ratio can be characterized by its average (3.52) and standard deviation (0.58 \approx 17%). The relative standard deviation of the signal area itself (measured at 45°) is about 50%, which indicates that the area ratio is the more consistent parameter for a monodisperse aerosol. This result suggests that the area ratio is indeed independent of particle trajectory. The average area ratio has been calculated for each of the recorded data sets and the results are plotted in Figure 10, as a function of particle size. The plot also contains the theoretical curve for corn oil, calculated from Mie theory. It is obvious



FIGURE 8 Longitudinal cross section of the aerosol beam generator.

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 focusing of the laser beam will cause the angle of incidence to vary, which can be incorporated in the calculations by averaging the signal over a small interval around the scattering angle. It is not clear, though, whether this smoothing effect is strong enough to produce an unique relationship between particle size and area ratio. In conclusion it can be stated that although the area ratio is constant for monodisperse particles, it is not easy to use a measure for particle size.

Peak Width

The results for a collection of monodisperse particles display a strong variation in peakwidth because of the intensity ambiguity problem. As a result, peak width is not



FIGURE 9 Histogram of the signal amplitude distribution measured for a population of 430 corn oil particles ($4 \mu m$ diameter).



FIGURE 10 Area ratios from the light scattering experiments (symbols) and Mie theory (lines).

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, by looking at the maximum peak width at maximum amplitude. 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. The results for ten data sets are plotted in Figure 11, as the reciprocal values, which is proportional to the terminal velocity. It should be noted that the exact numbers are not very reliable, because of the method through which they were determined. The limited number of data points available makes it difficult to obtain



FIGURE 11 Reciprocal peakwidth (proportional with the terminal velocity) as a function of particle size. The error bars indicate a 10% error in measured peak width.

reliable values. The figure shows that the reciprocal peak width decreases with particle size. This is consistent with observations by Dahneke (1973, 1974, 1978) and Prather *et al.*, 1994). Furthermore it is clear that the difference in mass density between polystyrene latex and corn oil (1050 and 920 kg/m^3 respectively) has little influence. These observations indicate that the peak width is linked to the particle terminal velocity. If the spread in peak width 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. Alternatively, the terminal velocity can be found by measuring the flight time of a particle as it crosses the beams of two lasers. This method is well-known, and it has been applied in commercial particle sizers like the APS 33B (TSI) and the API Aerosizer (Malvern).

PHOTO-IONIZATION TIME-OF-FLIGHT MASS SPECTROMETRY

Triggering

The chemical analysis of the particles involves vaporization by a pulsed Nd: YAG laser (Lumonics model HY1200) and ionization of the fragments. By using the frequency quadrupled radiation of this laser both processes can be induced at the same time. The flashlamps of the Nd: YAG laser are operated at a fixed frequency of 10 Hz, and the Q-switch is triggered by the light scattering process. When the two detectors simultaneously produce a signal exceeding a threshold level and the flash lamps are charged, a trigger signal is sent to the Q-switch, which opens to release a short pulse of intense radiation. The ions produced from a particle are sent into the flight tube of the mass spectrometer using a two-stage ion source. A digital oscilloscope records the ion flight times, which can be converted into a mass spectrum.

Ion Formation

There is a limited number of publications dealing with ion formation from airborne particles available in literature. Most of these are only attempts to explain the phenomenon of laser induced air breakdown and the role that aerosol particles play in this process. The paper by Armstrong (1984) is an exception, as it is aimed at describing the heating and vaporization processes that occur when a particle is irradiated by a strong laser beam. In addition to a simple model description of the steady state vaporization process, Armstrong also gives an equation for predicting the threshold intensity above which plasma formation can take place:

$$I_p \approx 4\rho c_0 E_I \tag{4}$$

An alternative approach is suggested by Vertes *et al.* (1989, 1989i), who define the plasma formation threshold as the point where the optical absorption by the plasma surpasses the absorption by the bulk material. By applying the concept of local thermal equilibrium a set of equations is obtained, which can be solved iteratively. Calculations for transparent and absorbing materials yield threshold intensities in the range from 4×10^{13} to 10^{15} W/m². These intensities are easily achieved with the pulsed laser used in the present study. Both experimental results and literature sources indicate that in this case strong fragmentation takes place, resulting in predominantly small ions.

Spectra

Mass spectra have been measured for a number of organic and inorganic compounds. At present, a mass resolution of 110 at 83 Da has been demonstrated. This value is too low to enable the routine analysis of organic compounds, and improvement of the resolution is therefore necessary. Examples of single particle spectra from ascorbic acid and from a mixture of inorganic salts are shown in Figure 12. The bottom spectrum clearly shows that cluster ions are frequently found when inorganic compounds are analyzed. Clusters like $(Na)_2^+$ and $(Na)_2Cl^+$ are quite common, and they are also found in experiments with conventional laser microprobe mass spectrometers like the LAMMA-500. With these instruments it is also possible to measure larger clusters, e.g. composed of three sodium ions and two chlorine ions. In the present experiments these cluster ions were rarely found, probably due to the high laser intensity.

It was unexpected that the particles containing a mixture of NaCl, KCl and $(NH_4)_2$ SO₄ did not produce any significant signals from the third compound, ammonium sulphate. In contrast, experiments with pure ammonium sulphate particles did produce proper mass spectra (Fig. 13). This observation indicates that the formation of ions from ammonium sulphate is suppressed by the more easily ionized alkalihalides (matrix effects). The ascorbic acid spectra 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_3O^+ (19), $C_2H_5^+$ (29), and CH_3O^+ (31). Na⁺ (23) is present as an impurity. The difference suggests that photo-



FIGURE 12 Mass spectra from single particles composed of ascorbic acid (top) and a mixture of NaCl, KCl and $(NH_4)_2SO_4$ (bottom).

ionization with an intensity in the order of 3×10^{14} W/m² (estimate based on a pulse energy of 1 mJ and a focal diameter of $20 \,\mu$ m) produces much stronger fragmentation than conventional ionization by electron impact. The theoretical thresholds calculated earlier suggest that plasma formation is possible with the applied intensity, which could be an explanation for the observed fragmentation.

If the instrument is to be applied successfully, it is essential that the mass spectra are reproducible. In order to quantify reproducibility, 30 spectra from pure sodium chloride were investigated. 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



FIGURE 13 Mass spectrum recorded from a single (NH₄)₂SO₄ particle.

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.
- 2 Due to the nature of the photo-ionization process the kinetic energy of the ions formed will vary from shot to shot. This effect will influence the ion flight time.
- 3 Temporal jitter in the electronics of either the laser or the triggering circuit, will directly influence the flight-time spectra.

Of the three factors listed above only the first one can be dealt with. Improvements can be expected from decreasing the focal size of the vaporization/ionization laser. An alternative method for quantifying 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 respective average values. The distribution of the deviation from the mean was plotted in a histogram, and the result is reproduced as Figure 14a. The described procedure was also applied to the sodium chloride spectra obtained with the present setup and the results are shown in Figure 14b. 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. It is expected that the reproducibility can be improved through optimization of the ionization process and fine-tuning of the mass spectrometer. In conclusion, 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 will influence the reproducibility of the spectra, but up to what extent is unknown.



FIGURE 14 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).

INSTRUMENT PERFORMANCE

The aerosol beam generator developed as the inlet of the instrument effectively transports particles to the analysis section. The transport efficiency varies with particle size, and values exceeding 90% have been demonstrated (Kievit, 1995). It is shown that particles with a diameter smaller than $2 \mu m$ are best sampled using a straight nozzle geometry (B in Fig. 4). For particles larger than $2 \mu m$ a convergent nozzle geometry (A in Fig. 4) has the highest efficiency. With a nozzle diameter of 0.3 mm the pressure at the ion source can be reduced to 3×10^{-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. The latter method has the advantage that it has been applied successfully in a number of commercially available instruments.

It is possible to use the scattering signals to trigger the vaporization and ionization laser and produce mass spectra. 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. With the Nd: YAG laser, the intensity of the photoionization pulse is estimated to be in the order of 3×10^{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. Conclusively, further research is expected to clarify the issue of matrix effects, and most likely increase the knowledge of the ionization process itself.

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NOMENCLATURE

Roman Symbols

 c_0 Local speed of sound (m/s) C_1, C_2 Empirical constants (-)

- C_c Cunningham slip correction factor (-)
- C_D Drag coefficient (-)
- Particle diameter (m)
- d_p D Nozzle diameter (m)
- E_I Ionization energy (J/kg)
- F_D Drag force (N)
- $I_p^ L_c^-$ Threshold intensity for plasma formation (W/m^2)
- Characteristic length of the barrel shock (m)
- Pressure downstream from the nozzle (Pa) pь
- Pressure upstream from the nozzle (Pa) p_0
- Velocity of the particle relative to the fluid (m/s) u_{rel}
- Distance between the nozzle and the point where the barrel shock has its X_{R} maximum radius (m)
- Distance between the nozzle and the Mach disk (m) Х_М
- Distance between the nozzle and the edge of the jet boundary (m) x_R
- Maximum diameter of the barrel shock (m) y_B
- Diameter of the Mach disk (m) Ум
- Diameter of the jet boundary at its edge (m) y_R

Greek Symbols

- Specific heat-ratio ($\gamma \equiv c_p/c_v$) γ
- Solid bulk density (kg/m^3) ρ

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