

PROPOSED ON-LINE AEROSOL ANALYSIS COMBINING SIZE DETERMINATION,
LASER-INDUCED FRAGMENTATION AND TIME-OF-FLIGHT MASS SPECTROSCOPY

Jan Marijnissen, Brian Scarlett and Peter Verheijen
University of Technology Delft
Dept. of Chemical Engineering
P.O. Box 5045, Delft
The Netherlands

Introduction

The aim of this work is the development of an instrument to analyze the size and chemical composition of individual aerosol particles "in-situ," on a continuous and real-time basis. It is anticipated that its applications include aerosol research, monitoring on behalf of environmental and health effects, clean-room technology and monitoring of production processes.

So far research on real-time determination of chemical composition focussed on the volatilization of individual particles with a hot filament, miniature oven or laser beam. The fragments are then analyzed with a quadrupole or focal plane mass spectrometer (Sinha *et al.*, 1982, 1984, 1986). The University of Technology Delft, the Netherlands has started a program whereby this approach is improved, extended and combined with "in-situ" particle size determination.

Instrumentation

Figure 1 shows the set-up of the proposed apparatus. A beam of aerosol particles (1) is generated by expanding the aerosol through a capillary into an evacuated chamber (2). An aerosol particle then passes first through a low-energy laser beam (3). The scattered light provides the size information and triggers instantaneously a pulsed power laser (YAG) (4). The laser pulse vaporizes and partially ionizes the fragments of the incident particle. A third laser (UV) (5) is planned to enhance the ionization. The resulting ions are analyzed by a time-of-flight (TOF) mass spectrometer (6). Processing of the large amount of spectra and size information needs to be done with an on-line computer (7).

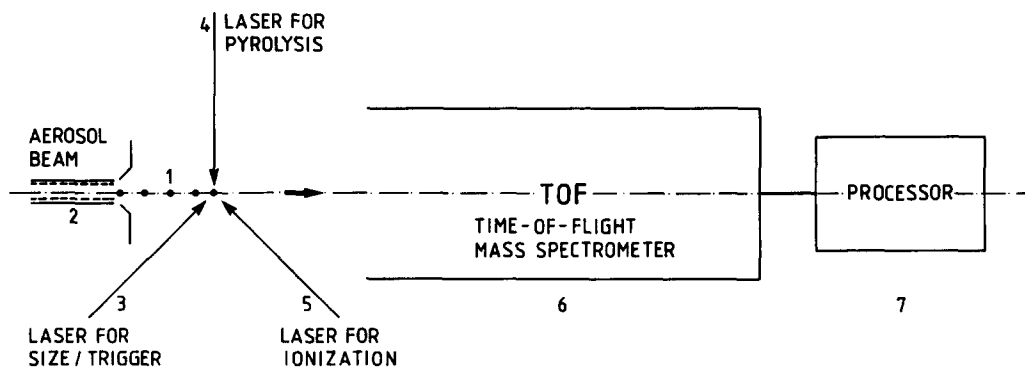


Fig. 1: Outline of the proposed apparatus for simultaneous size and mass analysis.

The only other comparable apparatus reported in the literature (Sinha, 1984) has a quadrupole mass spectrometer suitable for only one

mass at a time. Kaufmann (pers. comm.) has recently proposed an apparatus - for mobile monitoring - to be developed around the TOF mass spectrometer of the LAMMA, which detects a complete mass range and has a higher efficiency. The LAMMA (Vogt *et al.*, 1981) is a commercial apparatus for surface analysis, combining laser volatilization with TOF mass spectroscopy.

The essential improvement that we have included above, is letting the YAG-laser flash freely and only release a pulse through Q-switching, when a particle is detected during this flash. In principle this allows timing in the nanosecond range, and secures focussing of the power laser on the target particle with an accuracy on the orders of micrometers. This removes the necessity of separating the position of size measurement (Fig. 1 at (3)) from the position of pyrolysis (Fig. 1 at (4)), which would have been several centimeters (Sinha, 1984), as the particles are drawn into vacuum with a speed of 200 to 300 m/s.

Experiments/results

In cooperation with FOM (Netherlands Institute for Fundamental Research of Matter) the apparatus is being built at present and tests on different parts of the system are in progress to assess its usefulness. Inspection of a particle size laser has shown that signals from scattered light give the possibility to trigger a YAG laser with delays in the nanosecond range.

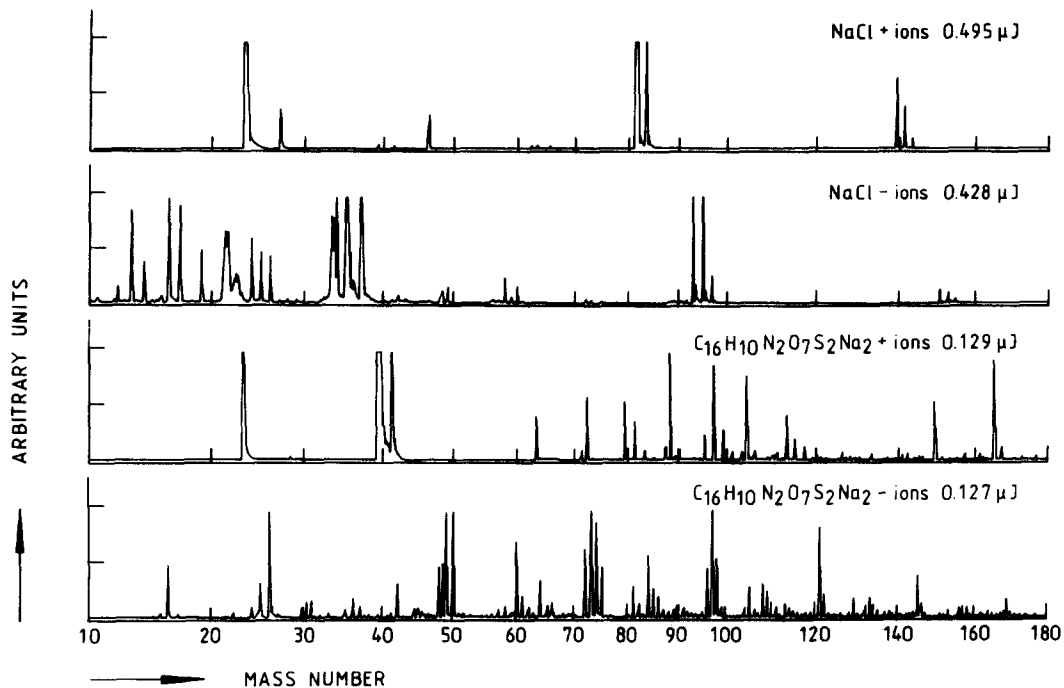


Fig. 2: Examples of Time-of-Flight mass spectra.

Samples of aerosol material have been analyzed by insertion in a LAMMA analyzer (by courtesy of Leybold). Considered are both inorganic and organic materials, different laser energies and both positive and negative ion-spectra (Fig. 2).

A key problem is the reproducibility. Firstly, the mass spectrum contains many species, partly from ionized molecules and partly from

clusters of ions with molecules. This makes an unambiguous identification impossible. Secondly, it is known that the LAMMA technique is more used as a method to detect compounds in aerosols, rather than to give a measure for the quantity present. For example, the peak height of a certain mass in a mass spectrum can vary typically with 20 % (Fig. 3), when the experiment is repeated under exactly the same circumstances. A deviation of 100 % between peak heights of two consecutively observed spectra are not uncommon.

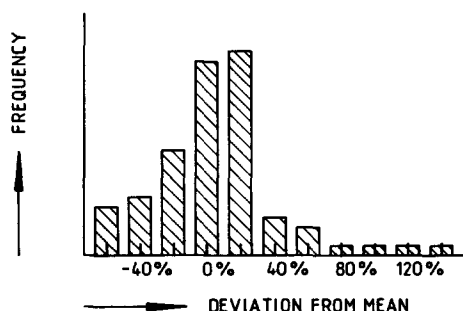


Fig. 3: Distribution of peak heights from TOF mass spectra. The abscissa is the deviation of the peak height, at one mass, from its average over a number of spectra.

Discussion and conclusion

Experiments and literature indicate that the proposed apparatus is realistic. The expected advantages of the system are the combination of size and chemical analysis of the individual particles, the creation of a complete mass spectrum per particle and the increased detection efficiency by using an extra ionizing laser beam. A disadvantage is that the aerosols necessarily have to be directed through vacuum because of the mass spectrometer.

The first experiments after commissioning the apparatus will be to investigate, whether volatilization and ionization of free particles make more reproducible mass spectra than the LAMMA, in which samples are mounted on a substrate and where operator handling also plays a role. If this is the case, as is intuitively expected, then extra quantitative value is added in comparison with the LAMMA. Kaufmann (pers. comm.) also expects that the extra ionizing laser will make the ionization complete, such that the fluctuations due to incomplete ionization might be eliminated.

A second line of research is the optimization of instrumental parameters, especially the laser pulse energy, in order to study different aspects of the aerosols. For example, it should be possible to investigate only surface adsorbed materials on aerosols with low laser energies or do complete bulk pyrolysis with high laser energies (for particles of 1 micrometer and smaller). As such this apparatus opens up new and as yet hardly explored avenues of basic aerosol research.

Thirdly, the apparatus will be used to collect mass spectra as a function of particle size and to develop computational techniques to compare them with reference distributions. This is useful for monitoring effluent from industrial processes or to observe ambient aerosols.

Finally, it is envisaged that this apparatus is used in observing time-dependent particle formation processes, including those of aerosols.

References

- Sinha, M.P., Giffin, C.E., Norris, D.D., Estes, T.J., Vilker, V.L., and Friedlander, S.K. (1982) "Particle Analysis by Mass Spectrometry" J. Coll. Interface Sci., 87, 140-153.
- Sinha, M.P. (1984) "Laser-induced volatilization and ionization of microparticles" Rev. Sci. Instrum., 55, 886-891.
- Sinha, M.P., and Friedlander, S.K. (1986) "Mass Distribution of Chemical Species in a Polydisperse Aerosol: Measurement of Sodium Chloride in Particles by Mass Spectrometry" J. Coll. Interface Sci., 112, 573-582.
- Vogt, H., Heinen, H.J., Meier, S., and Wechsung, R. (1981) "LAMMA 500 Principle and Technical Description of the Instrument" Fresenius Z. Anal. Chem., 308, 195-200.