# Series 3800 Aerosol Time-of-Flight Mass Spectrometers with Aerodynamic Focusing Lens Technology

New!

*Determine size and chemical composition of individual particles with higher efficiency and analysis rate*

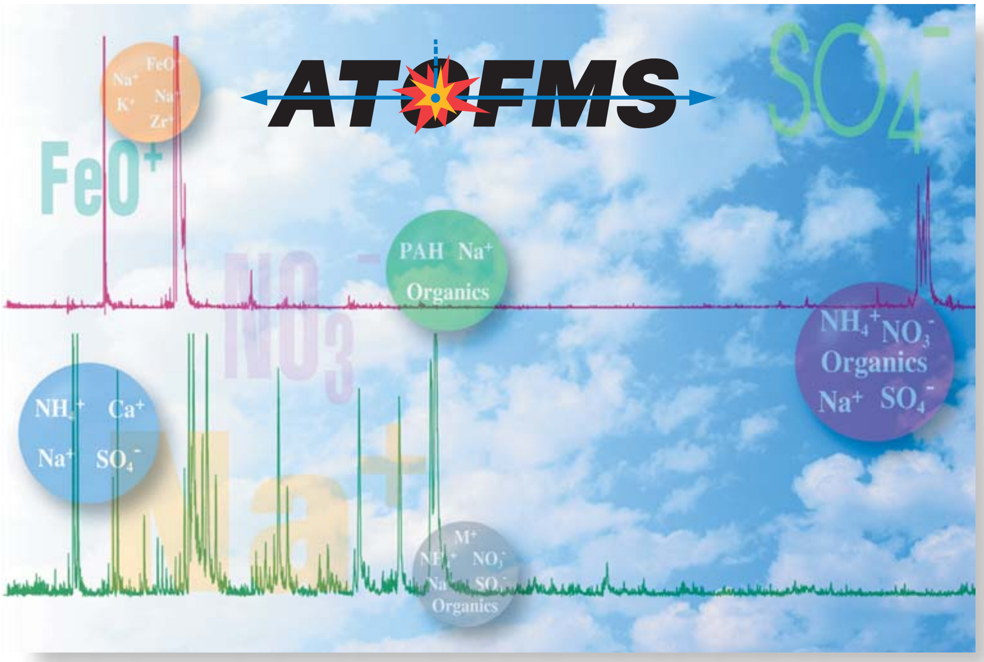
TSI introduces two new Aerosol Time-of-Flight Mass Spectrometers (ATOFMS) in the 3800 series of instruments with built-in Aerodynamic Focusing Lens technology. Without a focusing lens, the ATOFMS samples particles from a variety of sources through a nozzle. Typically, particles from about 100 to 3000 nanometers are sampled with sharply decreasing efficiency for smaller sizes. To overcome this size bias, to sample smaller particles efficiently, and to achieve an overall higher analysis rate for all sizes, TSI developed two new ATOFMS instruments with built-in Aerodynamic Focusing Lens technology.

Models 3800-030 and 3800-100 are mass spectrometers designed to effectively transmit particles in the size ranges 30 to 300 nanometers and 100 to 3000 nanometers, respectively. Transmission is close to 100 percent through the Aerodynamic Focusing Lens inlet.

## Introduction to ATOFMS

The Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) is a revolutionary instrument in the field of analytical chemistry. It offers great potential in areas such as atmospheric science, biological detection, pharmaceutical manufacturing, and engine research. Based on an instrument built by Prof. Kimberly A. Prather and her associates at the University of California, Riverside (Gard *et al.*), TSI's ATOFMS is the first single-airborne-particle mass spectrometer available commercially. Its transportable design allows it to be moved between measurement sites with minimal setup or reconfiguration, and it rolls through standard 36-inch-wide doorways. It also has a computer for data collection built inside the instrument cart.

Collectively, Series 3800 ATOFMS instruments provide single particle size and composition measurements in the size range from 30 to 3000 nanometers. They use an aerodynamic sizing technique that provides results similar to those obtained from a TSI




TSI®

Aerodynamic Particle Sizer® spectrometer. The aerodynamic size data serves as a timing trigger and calculates when each particle will be in the focal zone of an ablation laser. This laser desorbs and ionizes the particle for chemical analysis in a bipolar, time-of-flight mass spectrometer. Bipolar ion detection—where positive and negative mass spectra are obtained for each particle using separate ion detectors—gives you additional information about the particle and its source. Windows®-based software controls instrument functions and data acquisition.

Because the ATOFMS identifies the specific chemical compounds that make up each particle, it offers new insights into the dynamic chemistry between particles and surrounding gases, as well as other particles. Its nearly immediate composition analysis eliminates problems associated with traditional aerosol sampling onto a filter or impactor plate, such as possible secondary chemical reactions or losses of semivolatile compounds.

## Compound Analysis

Fragments of inorganic compounds formed during the ionization process are commonly made up of single elements and molecular ions, as well as cluster ions in an oxygen-rich atmosphere, containing one or two elements and oxygen. In particles containing transition metals, the oxide is typically present, too. The detection limit for sodium ions ($Na^+$) is $4 \times 10^{-16}$ mol with higher response for heavier alkali metals. This is consistent with periodic trends in both ionization potential and lattice energy (Gross *et al.*).

Many organic compounds give positive mass spectra that are similar to those found in libraries of 70-eV electron impact (EI) mass spectrometry (Silva and Prather). In comparison, protonated ions are expected from compounds containing polar functional groups. Negative mass spectra of organic compounds largely show carbon cluster fragments and contain fragments indicating the presence of electronegative ions such as oxygen and nitrogen.


ATOFMS shown without Aerodynamic Focusing Lens installed

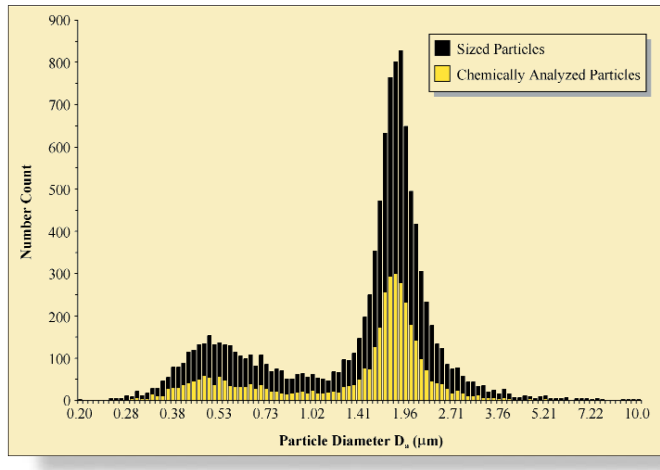
The many *polyaromatic hydrocarbons* (PAHs) have a large absorption cross-section because 266-nanometer light induces a resonant process. This leads to high sensitivity when compared to other organic compounds. The detection limit for PAHs is on the order of $10^{-18}$ mol (Morrical *et al.*).

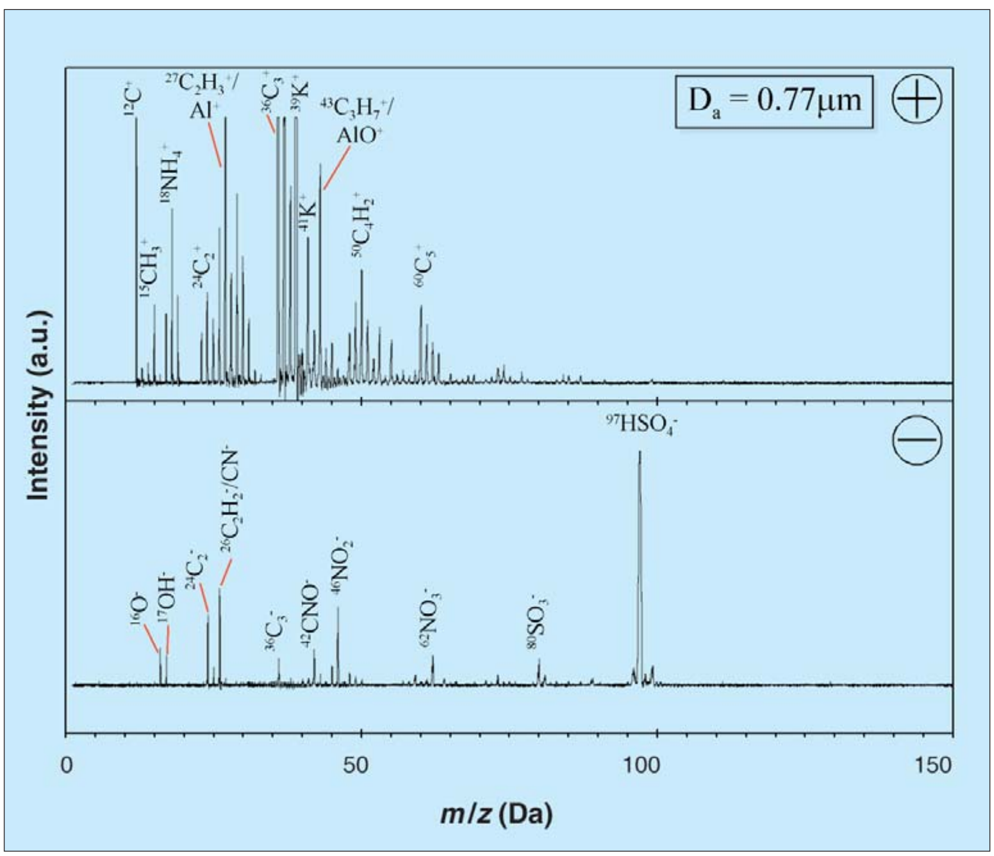
Extensive fragmentation may make it hard to distinguish between compounds in a particle containing many organics. However, it is often possible to determine specific classes of particles (PAHs, aliphatics, organic acids) based on a fingerprint or combination of peaks. The bipolar ion-analysis capabilities of the ATOFMS enhance the identification of several specific classes of compounds such as organic acids and salts.

## Applications

Series 3800 ATOFMS instruments determine single particle size and chemical composition in near real time. Applications include:

- Analytical aerosol research
- Atmospheric particle characterization, such as emission source identification
- Semiconductor processing
- Hard-disc-drive crash tests
- Indoor-air-quality monitoring
- Aerosolized-drug-delivery research
- Inhalation toxicology studies
- Drug-enforcement sample analysis
- Chemical and biological aerosol detection
- Engine emission measurements
- Powder manufacturing quality and process control for pigments, ceramics, polymers, pharmaceuticals, toners, and food powders




*The histogram above shows the qualitative particle size distribution of an ambient aerosol sample as measured by the ATOFMS (with no correction for particle losses). Detected particles appear in black; chemically analyzed particles in yellow. The mass spectra at left show the analysis of a single ambient organic particle taken from the same aerosol sample. Positive ions are displayed on top; negative ions on the bottom. The presence of peaks due to hydrocarbon clusters and potassium (*m/z *= 39 and 41) suggests that this particle was created by biomass burning. This is further supported by peaks in the negative spectrum at* m/z *= 26 ($CN^-$), 42 ($CNO^-$), 80 ($SO_3^-$), and 97 ($HSO_4^-$) (Silva* et al.*).*

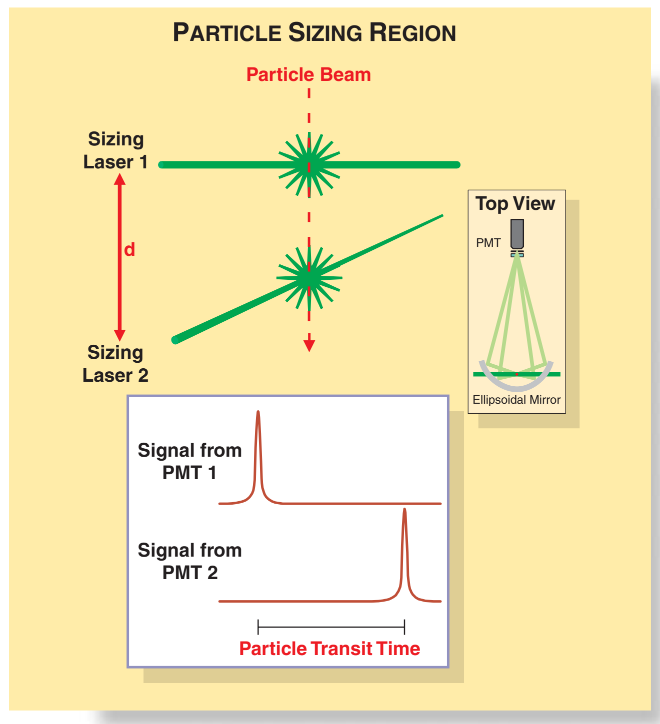
## Operation

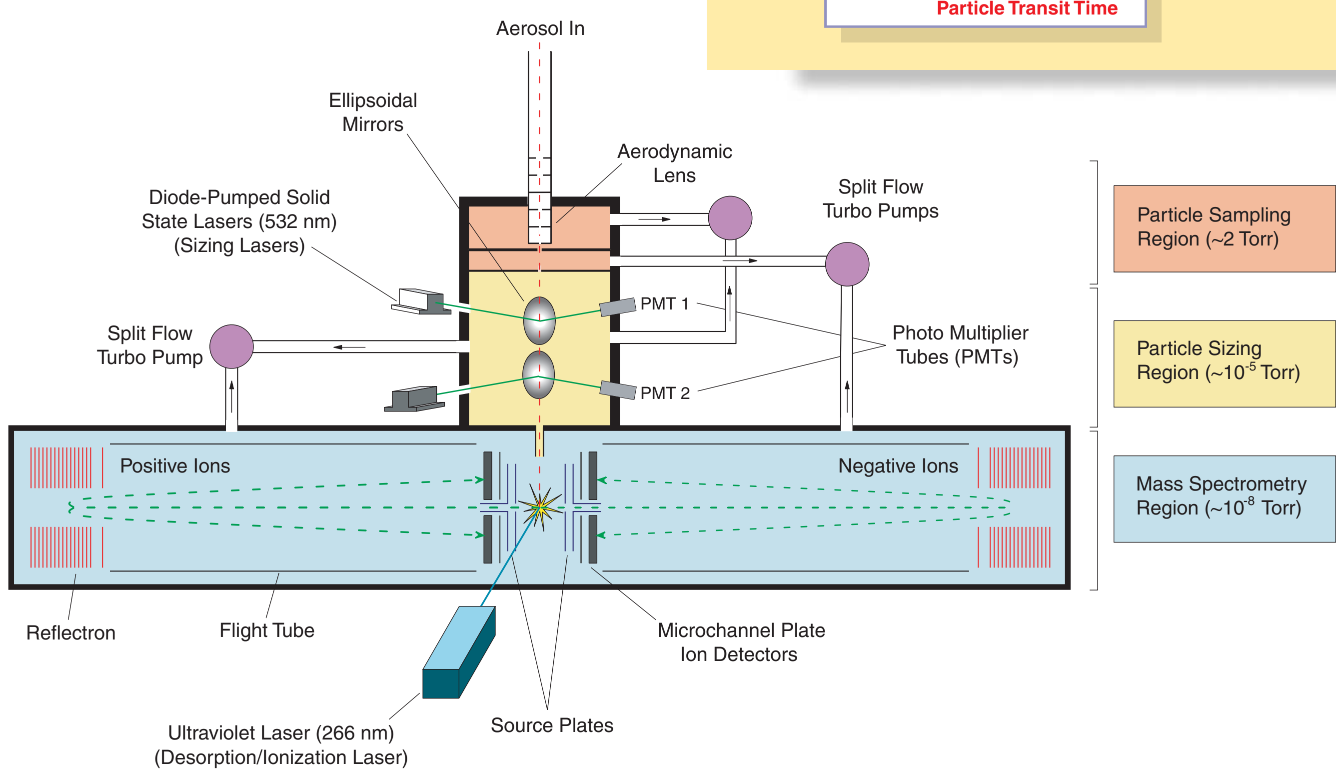
Series 3800 instruments employ two distinct time-of-flight technologies. One determines particle size; the other determines particle chemical composition. Gas-borne particles enter the ATOFMS inlet at atmospheric pressure (760 Torr).* A flow-limiting orifice reduces the pressure to a few Torr in the relaxation chamber, where particles are decelerated to reduce losses to the walls. The particles then travel through the Aerodynamic Focusing Lens (see details later) and exit through an accelerating nozzle. Due to their lower inertia, small particles accelerate more rapidly than large particles and obtain a higher terminal velocity during the expansion. After exiting the nozzle, the aerosol passes through two stages of differential pumping. This reduces the pressure to $10^{-4}$ Torr by the time the aerosol leaves the *particle sampling region*.

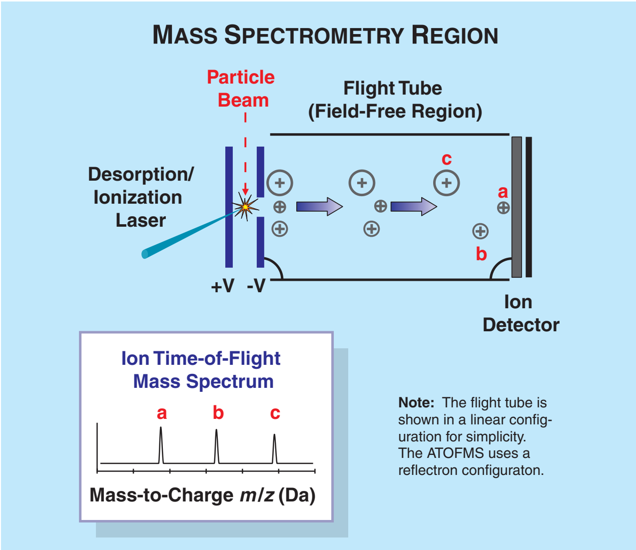
Once inside the *particle sizing region*, particles pass through a green, continuous-wave, diode-pumped solid-state (DPSS) laser beam, which generates an initial pulse of scattered light. A second DPSS laser, oriented orthogonally to the first, generates a second scatter pulse. The pulses are detected by two photomultiplier tubes (PMTs), one for each laser. The instrument determines particle velocity by measuring each particle's transit time between the two laser beams. This transit time is then translated into particle diameter based on an internally stored size calibration.

Next, the particles enter the *mass spectrometry region*, which is kept at a pressure of $10^{-7}$ Torr. The particle velocity measured in the particle sizing region is used to predict that particle's arrival at the ion source. A pulsed, ultraviolet laser fires, desorbing and ionizing the particle. The resulting ions are accelerated by positive and negative electric fields created by a series of source plates at different voltages. Ions with a lower mass-to-charge ratio ($m/z$) are accelerated to higher

*Pressure values discussed in this document are nominal.






velocities than ions with a higher ratio. The ATOFMS contains separate flight tubes for positive ions and negative ions. It measures the time-of-flight of both ion types as they travel from the ion source to their respective ion detector.

Reflectrons improve the spectral resolution of the instrument by compensating for any spread in the kinetic energy of the ions. Ions of the same *m/z* can have different kinetic energies due to different initial acceleration rates during the desorption and ionization process. High-energy ions travel faster than those of lower energy, but they stay in the reflectron for a longer period of time. As a result, ions of the same *m/z* arrive at the detector with less spread, which means improved mass spectral resolution. As a secondary benefit, the flight-path length is doubled (increasing the mass spectral resolution even further) without having to increase the length of the flight tubes, and therefore, the length of the instrument.

## The Aerodynamic Focusing Lens Technology

A flow-limiting orifice at the entrance to the relaxation chamber reduces the atmospheric pressure to operating pressure and sets the gas flow rate for the Aerodynamic Focusing Lens (AFL) system. The subsequent relaxation chamber forces the aerosol particles to decelerate, thereby minimizing wall losses. A precision bore tube holds a number of thin plate orifices (aerodynamic lenses), mounted in sequence with spacers between. The final exit aperture controls supersonic gas expansion and particle acceleration into the vacuum system. During the gas expansion, the particles acquire a distribution of velocities; smaller diameter particles accelerate to faster velocities and larger particles to slower velocities due to different particle inertia. The lens tube is mounted to the sizing region on ball-and-socket alignment surfaces (X-Y translation / tilt stage). This provides a means of aligning the beam for optimum transmission through the sizing region to the source region of the mass spectrometer.

## Aerodynamic Focusing Principle

Adjusting lens diameters and operating pressure alter the size range over which the AFL is effective. Due to the greater mass of particles compared to gas molecules, particles deviate from the streamlines of the expanding gas emerging from an aperture. Gas streamlines emerging from a circular lens element turn sharply from a perpendicular orientation to a parallel orientation relative the lens opening. The degree to which particles decouple from the streamlines is determined by the stokes number (St). Particles with St=0 follow the streamlines, while those with St>0 deviate from the streamlines. Particles with St close to 1 are confined closer to the centerline. A series of apertures inside the lens moves particles closer to the center axis after passing each individual aperture. By the time particles reach the nozzle, they are confined very closely to the center axis. In order to focus a wide range of particle sizes, the lenses become successively smaller in diameter.

Typically, five individual lenses in the 3- to 5-mm diameter range are sufficient to focus particles in the size range of one order of magnitude. The diameter of the particle beam measured 20 cm downstream of the accelerating nozzle is about 1 mm. The transmission efficiency for the lens is close to 100% over the full size range. It can be lower (>20%) through the entire instrument due to divergence in the beam and losses in the instrument.

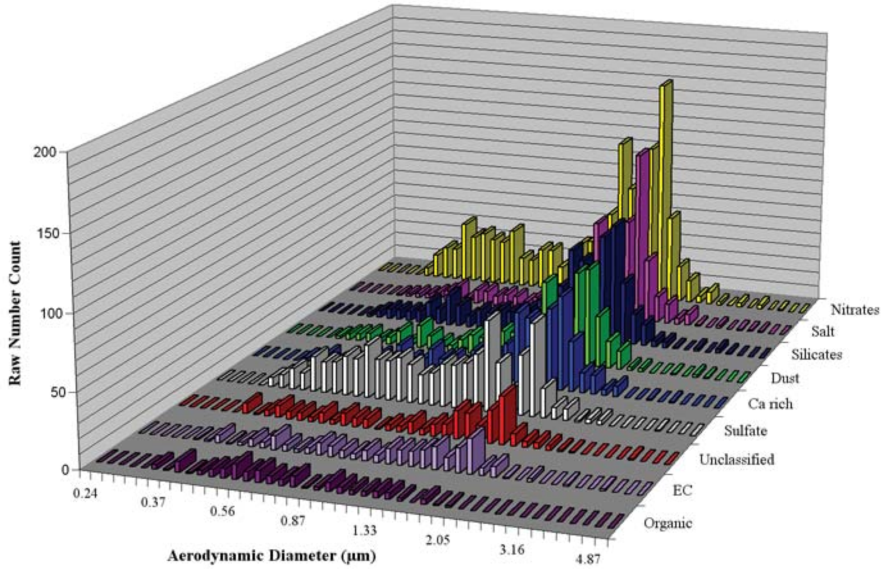
*The Aerodynamic Focusing Lens mounts on the ATOFMS inlet.*

## Operation of ATOFMS 3800-030

As particles below ~100 nm don't scatter enough light to be detected by the PMTs in the sizing region, aerodynamic sizing and triggering is not possible for these particles. Therefore, the instrument is run in "Free Fire" mode. This means that the UV laser is fired at its maximum repetition rate of 20 Hz and particles are hit based on statistical probabilities. The maximum hit rate can be calculated as

$$HR = n_{ae} \cdot V \cdot T \cdot D_L \cdot f \cdot E_a \cdot 1/v$$

with $n_{ae}$: number density of the aerosol, V: volume flow, T: inlet transmission efficiency, $D_L$: UV laser beam diameter, f: laser repetition frequency, $E_a$: ablation efficiency, and v: particle velocity (adapted from Kane and Johnston). In order to get size information, the aerosol has to be size-selected by using a Model 3080 Electrostatic Classifier with subsequent neutralization of the particles.




## Software

When running continuously, the ATOFMS typically generates 1 to 8 gigabytes of bipolar mass spectra and associated data per day. Therefore, effective analysis software is needed to process and store this large amount of data.

The ATOFMS uses two software packages, both of which are included with the instrument. The *MS-Control* operational software is a Windows®-based, $C^{++}$ program that controls instrument operation. It also displays and saves positive and negative spectra together with the associated size at a rate of up to 12 particles/sec. The *MS-Analyze* analytical software allows for analysis of the output from the MS-Control software. Particle size and related mass spectral data may be displayed through tables, graphs, and statistical lists.

MS-Analyze is based on a Microsoft® Access database, which allows for powerful searches in the acquired dataset. Particles may be classified based on the presence, absence, or intensity of specific peaks. The search may be limited to include only particles of a specific size range or sampling period, or within a certain ordinal count range. The "Watch Data Set" feature allows the user to analyze the acquired data in real time.

As size, mass spectra, and time of detection are recorded for each individual particle, size histograms for a whole dataset, for specific time windows, or for certain types of particles can be calculated. If classes are selected so that each particle can only belong to a single class (known as *exclusive classification*), pie charts displaying percentage composition of the whole sample can be generated from the data. Average spectra of selected classes, size ranges, or times may be calculated, as well.


*A 3-D histogram of an ATOFMS classification result is shown above. The computer screen at left shows an MS-Analyze workspace displaying windows with statistical data, classification results, hits and misses by the desorption/ionization laser over time, and a size distribution of hits and misses.*

## Specifications

### Series 3800 Aerosol Time-of-Flight Mass Spectrometers

| | |
|---|---|
| Particle Size Range† | |
| Model 3800-030 | 30 to 300 nm |
| Model 3800-100 | 100 to 3000 nm |
| Source Pressure | Atmospheric |
| Particle Type | Airborne solids and nonvolatile liquids |
| Display Resolution | Adjustable, up to 128 channels/decade, 257 channels total |
| Mass Range‡ | 1 to 800 Da |
| Resolution of Mass Spectra‡ | 500 m/Δm |
| Total Inlet Flow Rate (Volumetric) | 0.1 L/min |
| Operating Temperature | 10 to 35°C (50 to 95°F) |
| Storage Temperature | 5 to 50°C (40 to 120°F) |
| Operating Humidity | 0 to 75% RH, noncondensing |
| Maximum Operating Altitude | 2000 m (6562 ft) |
| Laser Sources | |
| Particle-sizing Lasers | 50 mW at 532 nm |
| Desorption/Ionization Laser | 5 mJ/pulse at 266 nm, maximum pulse rate of 20 Hz |
| Detectors | |
| Particle Size | Two photomultiplier tubes (PMTs) |
| Ion | Two microchannel plates (MCPs) |
| Dimensions (LWH) | 170 × 74 × 130 cm (67 × 29 × 51 in.) |
| Weight | 360 kg (790 lbs) |
| Power | 220 to 240 VAC, 50/60 Hz, 4 kW maximum |


## Acknowledgements

Series 3800 Aerosol Time-of-Flight Mass Spectrometer was developed under license from the University of California, Riverside, United States Patent Numbers 5,681,752 and 5,998,215. The Aerodynamic Focusing Lens technology is offered under license from University of Minnesota, United States Patent Number 5,270,542.

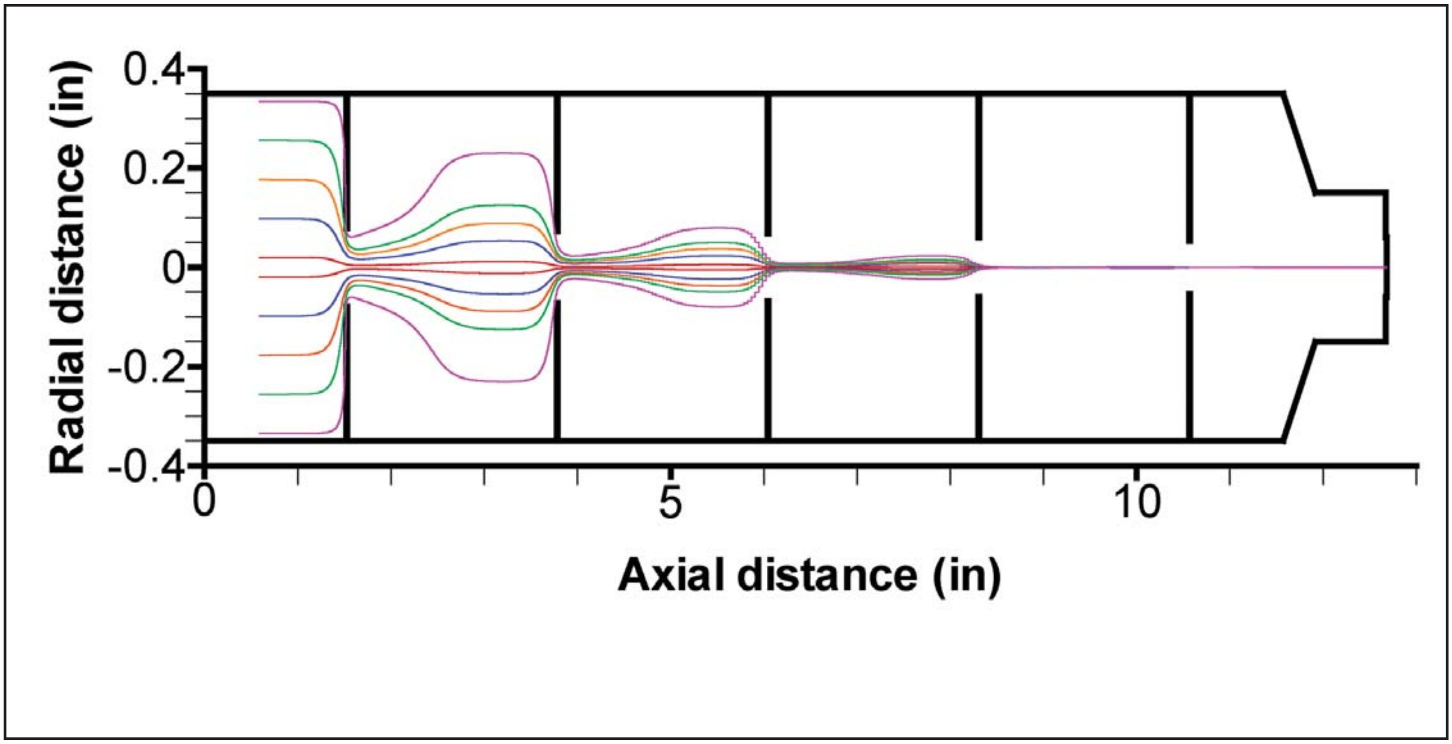

### To Order

**Aerosol Time-of-Flight Mass Spectrometer**

| *Specify* | *Description* |
|---|---|
| 3800-030 | ATOFMS and software for 30 to 300 nm |
| 3800-100 | ATOFMS and software for 100 to 3000 nm |

† Transmission efficiencies are dependent upon size.
‡ Mass range and resolution are dependent upon instrument conditions and settings.






*The interior of the Aerodynamic Focusing Lens (AFL) contains a series of indifidual, circular apertures that focus the aerosol flow.*

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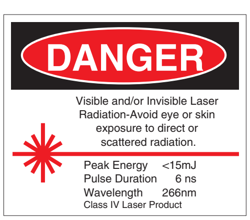



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