# Research

## Size and Chemical Characterization of Individual Particles Resulting from Biomass Burning of Local Southern California Species

PHILIP J. SILVA, DON-YUAN LIU, CHRISTOPHER A. NOBLE, AND KIMBERLY A. PRATHER\* Department of Chemistry, University of California, Riverside, California 92521

The chemical composition and size of individual particles derived from combustion products of several species found in Southern California were obtained using aerosol timeof-flight mass spectrometry. The major inorganic species observed in >90% of all biomass burning particles is potassium, indicated by the atomic ion, as well as clusters containing chloride, nitrate, and sulfate ions in the mass spectra. By obtaining positive and negative ion mass spectra it is possible to identify distinct chemical marker combinations in particles resulting from the burning of plant species, which in turn allows for differentiation from particles produced from other combustion sources such as vehicle emissions. Using these markers, particles derived from biomass burning were identified in ambient aerosol samples.

## Introduction

Various experimental and mathematical methods are currently being employed to determine the regional and global climate impact of atmospheric aerosols. Aerosols can affect the radiation balance of the earth both directly and indirectly depending on the size, chemical composition, and mixing state of single particles (1). Although sulfate aerosols are commonly considered the dominant anthropogenic contributor to tropospheric aerosols, smoke particles produced from biomass burning also play a significant role in the atmosphere in tropical regions, possibly impacting climate forcing as well as causing basic visibility problems in local areas (2-4).

Biomass burning includes both decisive and accidental clearing of forests, savannas, agricultural fields, and wood employed for cooking and heating (5). It is a significant contributor to particulate pollution around the world (6-8). A number of studies have been performed to characterize the emission rates and sizes of particles from combustion of biomass (9-13). Chemical composition information has been obtained for particles emitted from combustion of many types of biomass, including pine and oak wood (14), straw (15), several crop and wood fuels (16), and natural fires (17-20).

All of these previous studies were carried out using an off-line chemical analysis technique such as gas chromatography-mass spectrometry. Study of individual particles emitted by the combustion of various species can potentially provide useful information about possible chemical markers for real-time observation of the particles in the atmosphere. Furthermore, these chemical markers can be used to estimate more precisely the relative contribution of particles derived from biomass burning to atmospheric aerosols on a global scale.

The purpose of this paper is to obtain a qualitative chemical signature for biomass burning particles by analyzing the aerosol products of biota combustion. A number of species relevant to the Southern California area were tested to ensure applicability of the chosen markers as a general tool for identification of particles due to biomass burning as opposed to particles from other combustion sources. This analysis was performed on a single particle basis, measuring the size and chemical composition of each particle. To our knowledge, this is the first mass spectral study to determine chemical fingerprints for individual particles from biomass burning and then use these chemical markers in the analysis of particles in the atmosphere.

## **Experimental Section**

The analysis procedures used for this study are similar to those described in a recent paper (21). A variety of species of living biota were collected from the area surrounding the University of California, Riverside (UCR) campus. Particles from the combustion of biota were obtained by initiating the burning of various species with a Bunsen burner flame. The smoke emitted from the burning biota was collected in a glass sampling bottle. The container was then connected to the aerosol time-of-flight mass spectrometer by a copper transfer line. An HEPA Capsule Filter was attached to an inlet valve on the glass container. The filter allows particle free air to be pulled through the container to ensure a consistent flow into the instrument during analysis.

Aerosol time-of-flight mass spectrometry (ATOFMS) has been described in detail elsewhere (22-24). To date, ATOFMS has been employed for a variety of atmospheric analyses (25-28) and on-line source characterization (21). In ATOFMS analysis, a particle interface serves to introduce the particles into the instrument. Particles are collimated into a beam and accelerated to a final velocity that is proportional to their aerodynamic diameter  $(d_a)$ , with smaller particles proceeding at higher velocities. The particles then travel through a sizing region where the aerodynamic size of each individual particle is determined. In the sizing region, particles travel through two continuous-wave laser beams spaced a known distance apart. The light scattering signals produced as the particles travel through each laser beam are used to start and stop a timing circuit. This circuit records the flight time of each particle across this known distance, which is inversely proportional to its velocity. This velocity can be converted to an aerodynamic size using an appropriate calibration curve. At the time of this analysis, the instrument was calibrated down to a lower size limit of 0.3  $\mu$ m using polystyrene latex spheres. The timing circuit fires a Nd:YAG laser with a 266 nm pulsed output when the sized particle is present in the center of the ion source region of the mass spectrometer. Species present in the sized particle are desorbed and ionized, and the resulting positive or negative ions are detected in the mass spectrometer. The instrument has proven useful for determining size and chemical composition information of individual particles, even for complicated samples present in the atmosphere (25).

Samples were obtained from living plants in the area surrounding the UCR campus with an emphasis on areas prone to frequent fires. Samples were obtained from living



FIGURE 1. Size distributions of particles sampled from two different species of burning chaparral.

plants. For the shrub and tree samples, both leaves and branches were burned. For studies in this paper, each sample was burned as obtained, without controlling for factors such as humidity, water content, and sample thickness. It has been shown that emission rates can vary depending on these factors, which could lead to varying chemical composition (12). Emissions also can vary depending on whether the fire has flaming or smoldering characteristics (29). During the flaming phase of a fire, temperatures can reach hundreds of degrees centigrade. A fire in the smoldering phase exhibits temperatures closer to 50 °C. These temperature differences can alter the observed chemical composition of the emitted particles. For example, black carbon emissions decrease substantially between the flaming and smoldering phases of a fire (29). These factors will be controlled in future studies aimed at quantification.

Standards were analyzed using ATOFMS to determine some of the major compound(s) that contribute to observed peaks in the mass spectra. Commercial standards (Aldrich) were ground into a fine powder and suspended in a glass bottle as a pure component. The bottle was attached to the instrument and the samples were analyzed in a manner similar to the source samples. Operating conditions, such as laser power, were comparable to conditions for source sampling. A minimum of 100 individual particle mass spectra was obtained for each compound.

### Results

**Particle Size Distributions.** The combustion of biomass results primarily in the formation of accumulation mode particles ( $0.1 \,\mu$ m <  $d_a < 1 \,\mu$ m). This result is expected because it is known that small particles are derived from combustion sources (*30*). However, in this study, there was one exception to this general observation. One tree species produced coarse particles (defined in this work as  $d_a > 1 \,\mu$ m) in addition to fine particles ( $d_a < 1 \,\mu$ m). This observation is consistent with reports of coarse mode particles observed from natural wildfires (*31*).

Size distributions for particles emitted from two of the plant species during combustion are shown in Figure 1. The first size distribution is for particles emitted during the combustion of Red Prome, *Bromus madritensis var. rubens.* The size distribution of particles emitted during the combustion of this species shows that particles detected measured from 0.3  $\mu$ m up to 0.9  $\mu$ m, which is the typical size range of particles emitted during burning of the various plants. *Quercus suber* (Cork tree) was the one species that emitted coarse size particles. This cork tree species emitted particles during combustion that measured from the lower size limit of 0.3 up to ~1.4  $\mu$ m.

**Chemical Composition.** Figures 2-5 show the laser desorption/ionization (LDI) mass spectra from individual particles produced from the burning of four different plant species. Each figure shows a representative positive and negative ion mass spectrum acquired from the analysis of individual particles of a particular species. The dominant peak in all positive ion mass spectra for all species studied was mass-to-charge (m/z) 39 Da, which represents the potassium ion (<sup>39</sup>K<sup>+</sup>). Potassium was present in >90% of the positive ion mass spectra from all species studied.

From chemical analysis of the bulk aerosol, potassium is known to be a marker for particles produced by biomass combustion (32). Previous studies have shown that the concentration of potassium in PM2.5 smoke emissions ranges from 0.5% of the mass in softwood (14) to 16% of the mass for herbaceous fuels (16). These same studies report that the



FIGURE 2. Mass spectra of individual particles from *Bromus madritensis var. rubens.* (a) Positive ion spectrum of a 0.7  $\mu$ m particle. (b) Negative ion spectrum of a 0.3  $\mu$ m particle.



FIGURE 3. Mass spectra of individual particles from *Quercus suber*. (a) Positive ion spectrum of a 1.0  $\mu$ m particle. (b) Negative ion spectrum of a 1.1  $\mu$ m particle.



FIGURE 4. Mass spectra of individual particles from Ulmus parriflora. (a) Positive ion spectrum of a 0.6  $\mu$ m particle. (b) Negative ion spectrum of a 0.7  $\mu$ m particle.

next most concentrated metal is calcium at 0.02 and 0.08% of the mass, respectively. This study shows that the use of potassium as a chemical marker for biomass burning is valid on an individual particle level.

Also observed in the positive ion mass spectra are low intensity peaks that occur over a mass-to-charge range of several hundred Daltons. These peaks are due to molecular ions and fragments of the many organic compounds present in the particles. For the purpose of determining ambient markers of biomass burning particles, identification of all of these organic peaks is not required because the potassium ion and clusters, together with a few specific organic fragments, should be distinctive enough to allow tracking of biomass burning particles in the atmosphere. Negative ion mass spectra are also shown in Figures 2–5. Using the ATOFMS instrument, negative ion mass spectra generally

3070 • ENVIRONMENTAL SCIENCE & TECHNOLOGY / VOL. 33, NO. 18, 1999

do not provide as much information on chemical composition as do the positive ion mass spectra. However, negative ion mass spectra can provide more information on the presence of certain ions containing elements with a high electron affinity, such as oxygen, nitrogen, sulfur, and halogens.

In Figure 2, the positive and negative ion mass spectra of particles emitted during combustion of Red Prome are shown. This species is the dominant grass species present on the Box Springs Mountains that are often the site of wildfires adjacent to the UCR campus. Thus, the particles emitted from this species should be representative of particles observed in the atmosphere during local brushfires.

The positive ion mass spectrum is from a 0.7  $\mu$ m particle and shows the dominant peaks that are observed in the positive ion mass spectra of particles emitted from biomass



FIGURE 5. Mass spectra of individual particles from Salsola tragus. (a) Positive ion spectrum of a 0.6  $\mu$ m particle. (b) Negative ion spectrum of a 0.8  $\mu$ m particle.

burning. The spectrum contains sodium, potassium, and potassium clusters with other elements. The peak at m/z 39 Da is representative of  $^{39}$ K<sup>+</sup>. The area under the ion peak representing potassium makes up 20–50% of the total area of the ions in a typical mass spectrum for this species. The presence of sodium is indicated by the peak at m/z 23 Da. Several higher mass peaks are observed in the mass spectrum as well.

Almost all of the peaks observed in this spectrum are attributable to a cluster of potassium with a counter ion. The presence of a peak at m/z 104 Da is indicative of <sup>39</sup>K<sub>2</sub>CN<sup>+</sup>. The presence of cyanide clustered with potassium does not necessarily indicate that cyanide is present in the particle, because CN<sup>-</sup> can form due to the presence of carbon and nitrogen together in the particle (33, 34). Peaks at m/z 113 and 213 Da signify the presence of  ${}^{39}K_2{}^{35}Cl^+$  and  ${}^{39}K_2{}^{32}SO_4{}^+$ , respectively. These are the three most common potassium clusters that we observed in particles produced by biomass burning. Several other peaks are observed in the mass spectrum, although they occur in a smaller percentage of the mass spectra. Mass-to-charge ratios of 95, 120, 124, and 197 Da are commonly observed in these spectra. Based on the high potassium content of biomass burning aerosol and the isotopic distribution of potassium in the mass spectra, the most likely assignments to these peaks are <sup>39</sup>K<sub>2</sub>OH<sup>+</sup>, <sup>39</sup>K<sub>2</sub>-CNO<sup>+</sup>, <sup>39</sup>K<sub>2</sub>NO<sub>2</sub><sup>+</sup>, and <sup>39</sup>K<sub>3</sub>SO<sub>3</sub><sup>+</sup>, respectively.

A negative ion mass spectrum resulting from a 0.3  $\mu$ m particle is shown in Figure 2b. Four major peaks are observed, occurring at m/z 26, 42, 62, and 97 Da. These peaks correspond to CN<sup>-</sup>, CNO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and H<sup>32</sup>SO<sub>4</sub><sup>-</sup>, respectively. In the negative ion mass spectra of biomass burning particles, CN<sup>-</sup> was observed to be the dominant anion present. The large intensity of the peak due to CN<sup>-</sup> is consistent with the observation of potassium clustering with CN in the positive ion spectra at m/z 104 Da. The presence of the bisulfate ion was also common in the negative ion mass spectra. Nitrate was also observed in the mass spectra of the particles, though in a smaller percentage and lower intensity than CN<sup>-</sup> and H<sup>32</sup>SO<sub>4</sub><sup>-</sup>.

In Figure 3, the mass spectra of particles emitted from the combustion of bark from a Cork tree are shown. This is the species that displayed the size distribution indicating the presence of coarse mode particles ( $d_a > 1 \mu m$ ). A positive ion

mass spectrum resulting from a 1.0  $\mu$ m particle is shown in Figure 3a. In the mass spectrum, m/z 39 Da, corresponding to <sup>39</sup>K<sup>+</sup>, is once again the largest peak in the mass spectrum. However, the spectrum contains many additional high intensity peaks due to fragmentation of organic species. Several groups of peaks due to ions made up of carbon and hydrogen are observed. Mass-to-charge ratios of 12 and 15 Da are dominant in the first group of peaks, corresponding to C<sup>+</sup> and CH<sub>3</sub><sup>+</sup>, respectively. In the second group, m/z 27, 29, and 31 Da are the dominant peaks, which probably correspond to C<sub>2</sub>H<sub>3</sub><sup>+</sup>, C<sub>2</sub>H<sub>5</sub><sup>+</sup>, and CH<sub>3</sub>O<sup>+</sup>, respectively, although m/z 31 Da can also be P<sup>+</sup>. A group of peaks is also observed extending from m/z 36 Da (C<sub>3</sub><sup>+</sup>) to 43 Da (C<sub>3</sub>H<sub>7</sub><sup>+/</sup>, C<sub>2</sub>H<sub>3</sub>O<sup>+</sup>). The carbon-hydrogen envelopes continue out to about C<sub>9</sub><sup>+</sup>.

In Figure 3b, the negative ion mass spectrum resulting from analysis of a 1.1  $\mu$ m particle contains some unique markers that were observed in the mass spectra of almost all of the species that were burned. The presence of CN<sup>-</sup>, CNO<sup>-</sup>, and  $H^{32}SO_4^-$  is observed in this spectrum, as in Figure 2b. One also observes the presence of carbon-hydrogen envelopes in the spectrum, appearing out to  $C_{10}$ . Several noticeable peaks occur at m/z 45, 59, and 71 Da. These three peaks occur in a large percentage of the negative ion mass spectra of particles from biomass burning and do not occur in other organic particles from other sources that we have analyzed thus far. The assignments of the peaks at m/z 45 and 59 Da are most likely due to the formate (CHO<sub>2</sub><sup>-</sup>) and acetate ( $C_2H_3O_2^-$ ) ions, respectively. The peak at m/z 71 Da is most likely  $C_3H_3O_2^-$ , although it has other possible assignments.

The presence of these oxygen-containing peaks in both the positive and negative ion mass spectra can be indicative of many different oxygen-containing organic compounds present in a sample. Many oxygen-containing compounds have been identified in biomass burning particles using bulk aerosol analysis. Large concentrations of lignin combustion products, such as aromatic alcohols, aldehydes, and acids, have been identified in particles resulting from biomass burning (*35*).

Another compound that contributes to these negative ion peaks is levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose), which is a sugar that is a major product of the combustion



FIGURE 6. Mass spectra of individual particles of levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose). (a) Positive ion mass spectrum. (b) Negative ion mass spectrum.



FIGURE 7. Frequency of occurrence of positive ions in the mass spectra of biomass burning particles.

of cellulose (36). Levoglucosan was recently found to make up 18% of fine particle organic carbon emitted from the combustion of pine wood and 31% from eucalyptus wood (37). These mass emissions concentrations make levoglucosan a good candidate for a smoke marker. Figure 6 shows mass spectra obtained from analysis of levoglucosan powder. Each spectrum is an average of five individual particle mass spectra. The positive ion mass spectrum in Figure 6a displays common low mass organic fragments from m/z 12 to 43 Da. The negative ion mass spectrum exhibits major peaks at m/z45, 59, and 71 Da, similar to the source characterized particles. Other peaks observed in the negative ion mass spectrum include *m*/*z*41 Da (C<sub>2</sub>HO<sup>-</sup>), 58 Da (C<sub>2</sub>H<sub>2</sub>O<sub>2</sub><sup>-</sup>), 87 Da (C<sub>3</sub>H<sub>3</sub>O<sub>3</sub><sup>-</sup>), and a deprotonated parent ion at 161 Da (C<sub>6</sub>H<sub>9</sub>O<sub>4</sub><sup>-</sup>). These peaks, although present in some of the source characterized particles, do not have as much potential for markers because they are not solely distinctive of biomass burning particles, and in the case of m/z 161 Da, are not reproducible at all laser fluences.

Figure 4 shows the mass spectra of particles from the combustion of a third species. These particles resulted from



FIGURE 8. Frequency of occurrence of negative ions in the mass spectra of biomass burning particles.

the combustion of the leaves from a Chinese Elm tree, *Ulmus parriflora*. This cultivated tree species does not occur in the wild. It was studied to observe whether markers for the combustion of indigenous species would be valid for cultivated species.

The positive ion mass spectrum of a 0.6  $\mu$ m particle is shown in Figure 4a. The only major peaks are due to potassium. A peak at mass-to-charge 39 Da (39K+) is the largest peak in the spectrum. All other peaks are of low intensity and due to organic compounds and fragments. This mass spectrum shows that the presence of potassium is the only consistently reproducible inorganic marker present in the positive ion mass spectra of particles from the combustion of plant species. The negative ion mass spectrum resulted from analysis of a 0.7  $\mu$ m particle and is shown in Figure 4b. Only three major peaks, OH<sup>-</sup>, CN<sup>-</sup>, and CNO<sup>-</sup>, are observed. This mass spectrum shows that the presence of CN<sup>-</sup> is the only reproducible major marker peak seen in the negative ion mass spectra. Because the presence of any type of nitrogen-containing organic compounds in the particle can give rise to a CN<sup>-</sup> peak, this spectrum offers no specific



FIGURE 9. Positive ion mass spectra of individual particles from ambient air. (a) A 0.7  $\mu$ m particle sampled on September 29, 1996. (b) A 0.5  $\mu$ m particle sampled on September 29, 1996.



FIGURE 10. Negative ion mass spectra of individual particles from ambient air. (a) A 0.4  $\mu$ m particle sampled on July 11, 1996. (b) A 0.5  $\mu$ m particle sampled on September 24, 1997.

markers in negative ion mode when analyzing ambient particles for source allocation.

Figure 5 displays the mass spectra of particles resulting from the combustion of common Tumbleweed, *Salsola tragus*. This species exhibited a slightly different chemical composition than the other species. In this positive ion mass spectrum of a 0.6  $\mu$ m particle (Figure 5a), the presence of potassium is observed at m/z 39 Da. However, in this case, a peak at m/z 23 Da that represents sodium (Na<sup>+</sup>) is almost as large as the potassium peak. Numerous large peaks that are presumably due to organic fragments such as m/z 27 Da (C<sub>2</sub>H<sub>3</sub><sup>+</sup>) are observed.

There is a distinct difference between in this mass spectrum than in the previous positive ion mass spectra (Figures 2a, 3a, 4a). The appearance of peaks at m/z206, 207, and 208 Da are attributable to the three isotopes of lead,

with the largest occurring at m/z 208 Da (<sup>208</sup>Pb<sup>+</sup>). Lead was observed in 5% of the particles emitted from the combustion of this species of plant. The presence of lead could indicate the occurrence of particle deposition on the surface of the plant or an ability of the species to absorb lead from the ground. Although this species is extremely efficient at creating biomass and at absorbing nutrients from the ground (*38*), this particular sample was obtained near a roadway, so it is possible that deposition from particles emitted from automobile exhaust has occurred.

The negative ion mass spectrum from a particle due to combustion of tumbleweed is shown in Figure 5b. The particle measured 0.8  $\mu$ m in diameter. In the mass spectrum, large peaks are observed at m/z12, 16, 17, 26, 35, and 42 Da. These peaks correspond to the presence of C<sup>-</sup>, O<sup>-</sup>, OH<sup>-</sup>, CN<sup>-</sup>, <sup>35</sup>Cl<sup>-</sup>, and CNO<sup>-</sup>, respectively. In addition, a unique set of peaks



FIGURE 11. Temporal profile of the number concentration of brushfire particles sampled on July 2, 1997. Number concentration is reported as a percentage of the total particles sampled during a 15-min interval.

occurs from approximately m/z 117 to 131 Da. This unique envelope of peaks occurs reproducibly in 7% of the mass spectra of particles from this particular species. The mass spectra for the combustion of this species are also interesting because the peaks at m/z 45, 59, and 71 Da are completely absent from the mass spectra. This species is the only one studied for which the single particle negative ion mass spectra did not contain these three peaks.

A fifth species of plant was also studied. *Encelia farinosa*, commonly known as Incienso, is a desert shrub that is prevalent throughout Southern California (*39*) and makes up most of the ground cover on the nearby Box Springs

Mountains (40). The particles that were produced from the combustion of this species yielded mass spectra that were similar to the other species with >90% of the positive ion mass spectra showing the presence of potassium, and cyanide ion being the most common negative ion detected.

Figures 7 and 8 provide a summary of some of the ions that have been detected in the particles from biomass burning for positive and negative ion analysis, respectively. It is easy to see that potassium and potassium-containing clusters are the major inorganic species that are present in a large number of positive ion mass spectra from all of the species that were studied. Potassium is present in >90% of the mass spectra from particles emitted during the combustion of every species for which data were taken. Sodium is observed in a smaller percentage of the mass spectra from all of the species that underwent combustion. Lead is observed in the particles from the combustion of Tumbleweed. Cyanide, chloride, and sulfate are the most commonly observed anions in the particles emitted during combustion of biomass, but oxygencontaining ions present at m/z 45, 59, and 71 are distinct peaks that have not been observed in other particle types studied by ATOFMS to date.

**Atmospheric Aerosol Analysis.** Using the combination of positive and negative ion chemical composition information summarized in Figures 7 and 8, it is possible to identify the presence of particles resulting from biomass burning when sampling ambient outdoor aerosols. The identification of specific particle sources in atmospheric samples is necessary for eventual source allocation studies by our research group. Figures 9 and 10 show mass spectra of single particles that were taken by ATOFMS during ambient sampling. The mass spectra were recorded while a wildfire



FIGURE 12. Positive ion mass spectra of three particle types. (a) A 0.8  $\mu$ m particle derived from biomass burning. (b) A 1.8  $\mu$ m particle derived from suspended dust. (c) A 1.2  $\mu$ m sea salt particle.

burned on the Box Springs Mountains near the UCR campus. These spectra have been identified as being derived from fires in the area, based on the size and chemical composition information that the particles exhibited.

In Figure 9a, the positive ion mass spectrum is shown for a 0.7  $\mu$ m particle sampled at 5:47 p.m. on September 29, 1996. In the spectrum, large peaks at m/z 39 and 41 Da due to potassium are observed. Peaks corresponding to K<sub>3</sub>SO<sub>4</sub><sup>+</sup> are also observed at m/z213 and 215 Da. Other notable peaks in the mass spectrum include those that are due to organic species (C<sup>+</sup>, C<sub>3</sub><sup>+</sup>, and C<sub>4</sub>H<sub>2</sub><sup>+</sup>), as well as Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup>.

Another positive ion mass spectrum sampled from ambient air during the same wildfire is shown in Figure 9b. This particle is 0.5  $\mu$ m in diameter and was sampled at 6:11 p.m. on September 29, 1996. Larger peaks due to organic species are observed in this spectrum. The presence of C<sup>+</sup>, C<sub>2</sub><sup>+</sup>, and C<sub>3</sub><sup>+</sup> indicate the fragmentation of organic species. More important however, is the presence of potassium and potassium cluster peaks, once again indicating the source of this single particle. The presence of <sup>39</sup>K<sub>2</sub><sup>35</sup>Cl<sup>+</sup> at *m*/*z* 113 Da indicates that this particle is probably derived from biomass burning. Other potassium-related peaks that are observed are *m*/*z* 78 Da (<sup>39</sup>K<sub>2</sub><sup>+</sup>), and 94 Da (<sup>39</sup>K<sub>2</sub>O<sup>+</sup>).

In Figure 10a, a negative ion mass spectrum of a particle from biomass burning is shown. The mass spectrum of this particle was obtained during a different ambient sampling period. This 0.4  $\mu$ m particle was sampled at 11:53 p.m. on July 11, 1996. In this spectrum, the presence of CN<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> is observed. However, three other major peaks observed in the mass spectrum, *m*/*z* 45, 59, and 71 Da, are the three negative ion marker peaks identified in Figure 3b. These peaks strongly indicate that this individual particle was derived from the combustion of biomass.

In Figure 10b, a second negative ion mass spectrum for a single particle is displayed. This particle was analyzed at 11:33 p.m. on September 24, 1997, and measured 0.5  $\mu$ m in diameter. In the spectrum, major peaks are observed corresponding to C<sup>-</sup>, O<sup>-</sup>, OH<sup>-</sup>, CN<sup>-</sup>, and Cl<sup>-</sup>, as well as the biomass burning marker peaks at m/z 45, 59, and 71 Da.

By employing specific chemical markers evident in the single particle mass spectra, specific aerosol sources may be monitored in atmospheric samples. One example of biomass burning source identification is shown in Figure 11 for an ambient outdoor sampling. On July 2, 1997, a small brushfire occurred at Box Spring Mountains near the UCR campus during the late morning and early afternoon. Using an automated computer search algorithm, single particles were identified that contained an ion peak at m/z 213 Da ( ${}^{39}K_{3}{}^{32}SO_{4}{}^{+}$ ) for all particles sampled during this day. The total sample size was 34 000 particles.

The number concentration of these particles  $(N_{bb})$  is graphed as a relative percentage of all particles sampled during continuous 15-min intervals throughout the entire day. The arrival at the UCR campus of the particulate products of this brushfire occurs at a very obvious and distinct time, just after 9:00 a.m. The relative percentage of mass spectra containing m/z 213 Da is at a maximum from 12:00 to 1:30 p.m., during which time the atmospheric contribution due to the brushfire accounted for >5% of all particles sampled with the ATOFMS instrument. The relative concentration of these biomass burning particles decreases significantly by 2:00 p.m. Tracking a specific particle type with the time resolution shown here can not be accomplished without a single particle technique such as ATOFMS. Because the particles due to biomass burning are dominantly small particles (<1  $\mu$ m), they are undercounted by ATOFMS due to the low scattering efficiency of smaller sized particles. Current work in our laboratory aimed at correcting for this size biasing will allow for true quantitative analysis of the

relative contribution of biomass burning particles to atmospheric aerosols in the future.

Potassium by itself does not make an adequate marker for particles due to biomass burning because it is present in mass spectra of particles from a variety of different sources, including sea salt (25), tobacco smoke, soil, and smoke from meat cooking operations (41). However, the presence of potassium and cluster ions with chloride and sulfate allows definitive identification of particles derived from biomass burning versus sea salt or soil particles. This is displayed in Figure 12a-c, where positive ion spectra of a biomass burning particle, a soil particle, and a sea salt particle are shown, respectively. Recently, a new generation of field transportable ATOFMS instrumentation has been constructed (42). These instruments have bipolar ion detection for the mass spectral analysis, allowing for the collection of both positive and negative ion spectra from a single particle. The combination of both ions allows for conclusive identification of biomass burning particles versus other combustion-related particles, such as tobacco smoke, because the presence of peaks at m/z 45, 59, and 71 Da are solely distinctive of particles due to biomass burning.

### Acknowledgments

The authors thank Dr. David Weise of the USDA Forest Service, Pacific Southwest Research Station, Dr. Andrew Sanders of the University of California, Riverside Botanical Gardens, and Dr. Jamie Schauer of the California Institute of Technology for technical support throughout this work. This research was supported by grants CHE-9457680 and CHE-9412317 from the National Science Foundation.

#### Literature Cited

- Pilinis, C.; Pandis, S. N.; Seinfeld, J. H. J. Geophys. Res. 1995, 100, 18739–18754.
- (2) Penner, J. E.; Dickinson, R. E.; O'Neill, C. A. Science 1992, 256, 1432–1434.
- (3) Hobbs, R. V.; Reid, J. S.; Kotchenruther, R. A.; Ferek, R. J.; Weiss, R. Science 1997, 275, 1776–1778.
- (4) Kaufman, Y. J.; Fraser, R. S. Science 1997, 277, 1636-1639.
- (5) Levine, J. S.; Cofer, W. R., III.; Cahoon, D. R., Jr.; Winstead, E. L. Environ. Sci. Technol. 1995, 29, 120A–125A.
- (6) Duce, R. A. Pure Appl. Geophys. 1978, 116, 244-273.
- (7) Seiler, W.; Crutzen, P. J. Clim. Change 1980, 2, 207-247.
- (8) Schauer, J. J.; Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. Atmos. Environ. 1996, 30, 3838– 3855.
- (9) Stith, J. L.; Radke, L. F.; Hobbs, P. V. Atmos. Environ. 1981, 15, 73-82.
- (10) Brown, J. K.; Bradshaw, L. S. Int. J. Wildland, Fire **1994**, 4, 143–155.
- (11) Brauer, M.; Bartlett, K.; Regaldo-Pineda, J.; Perez-Padilla, R. *Environ. Sci. Technol.* **1996**, *30*, 104–109.
- (12) Weise, D. R.; Ward, D. E.; Paysen, T. E.; Koonce, A. L. Int. J. Wildland Fire 1991, 1, 153–158.
- (13) Hardy, C. C.; Conard, S. G.; Regelbrugge, J. C.; Teesdale, D. R. USDA Research Paper PNW-RP-486, 1996.
- (14) Hildemann, L. M.; Markowski, G. R.; Cass, G. R. Environ. Sci. Technol. 1991, 25, 744-759.
- (15) Christensen, K. A.; Livbjerg, H. Aerosol Sci. Technol. 1996, 25, 185–199.
- (16) Turn, S. Q.; Jenkins, B. M.; Chow, J. C.; Pritchett, L. C.; Campbell, D.; Cahill, T.; Whalen, S. A. J. Geophys. Res. 1997, 102, 3683– 3699.
- (17) Veltkamp, P. R.; Hansen, K. J.; Barkley, R. M.; Sievers, R. E. Environ. Geochem. Health 1996, 18, 77–80.
- (18) Gaudichet, A.; Echalar, F.; Chatenet, B.; Quisefit, J. P.; Malingre, G.; Cachier, H.; Buat-Menard, P.; Artaxo, P.; Maenhaut, W. J. Atmos. Chem. 1995, 22, 19–39.
- (19) Cachier, H.; Liosse, C.; Buat-Menard, P. Gaudichet, A. J. Atmos. Chem. **1995**, *22*, 123–148.
- (20) Abas, M. R.; Simoneit, B. R.; Elias, V.; Cabral, J. A.; Cardoso, J. N. Chemosphere 1995, 30, 995–1015.
- (21) Silva, P. J.; Prather, K. A. Environ. Sci. Technol. 1997, 31, 3074– 3080.

- (22) Prather, K. A.; Nordmeyer, T.; Salt, K. Anal. Chem. 1994, 66, 1403–1407.
- (23) Nordmeyer, T.; Prather, K. A. Anal. Chem. 1994, 66, 3540–3542.
  (24) Noble, C. A.; Nordmeyer, T.; Salt, K.; Morrical, B.; Prather K. A.
- *Trends Anal. Chem.* **1994**, *13*, 218–222. (25) Noble, C. A.; Prather, K. A. *Environ. Sci. Technol.* **1996**, *30*, 2667–
- 2680.
  (26) Liu, D.-Y.; Rutherford, D.; Kinsey, M.; Prather, K. A. Anal. Chem.
  1997, 69, 1808–1814.
- (27) Noble, C. A.; Prather, K. A. Geophys. Res. Lett. 1997, 24, 2753–2756.
- (28) Gard, E. E.; Kleeman, M. J.; Gross, D. S.; Hughes, L. S.; Allen, J. O.; Morrical, B. D.; Fergenson, D. P.; Dienes, T.; Gälli, M. E.; Johnson, R. J.; Cass, G. R.; Prather, K. A. *Science* **1998**, *279*, 1184–1187.
- (29) Susott, R. A.; Ward, D. E.; Babbitt, R. E.; Latham, D. J. In *Global Biomass Burning*; MIT Press: Cambridge, MA, **1991**; pp 245–257.
- (30) Finlayson-Pitts, B. J.; Pitts, J. N. Jr. In Atmospheric Chemistry: Fundamentals and Experimental Techniques; John Wiley & Sons: New York, 1986; Chapter 12.
- (31) Radke, L. F.; Hegg, D. A.; Hobbs, P. V.; Nance, J. D.; Lyons, J. H.; Laursen, K. K.; Weiss, R. E.; Riggan, P. J.; Ward, D. E. In *Global Biomass Burning*; MIT Press: Cambridge, MA, **1991**; pp 209–224.
- (32) Andreae, M. O. Science 1983, 220, 1148-1151.

- (33) Mauney, T.; Adams, F.; Sine, M. R. Sci. Total Environ. 1984, 36, 236–240.
- (34) Kolaitis, L. N.; Bruynseels, F. J.; Van Grieken, R. E.; Andreae, M. O. *Environ. Sci. Technol.* **1989**, *23*, 236–240.
- (35) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.* **1998**, *32*, 13–22.
- (36) Lomax, J. A.; Boon, J. J.; Hoffman, R. A. Carbohydr. Res. 1991, 221, 219–233.
- (37) Schauer, J. J. Ph.D. Thesis, California Institute of Technology, Pasadena, California, 1998.
- (38) James, D. Arid Lands Newsletter 1996, 37, 1.
- (39) Belzer, T. J. Roadside Plants of Southern California; Mountain Press: Missoula, MT, 1984; p 78.
- (40) Sanders, A. C. University of California at Riverside Botanical Gardens, personal communication, 1997.
- (41) Prather, K. A. University of California at Riverside, unpublished results.
- (42) Gard, E.; Mayer, J. E.; Morrical, B. D.; Dienes, T.; Fergenson, D. P.; Prather, K. A. Anal. Chem. 1997, 69, 4083–4091.

Received for review May 27, 1998. Revised manuscript received May 18, 1999. Accepted June 7, 1999.

ES980544P