Relative Sensitivity Factors for Alkali Metal and Ammonium Cations in Single-Particle Aerosol Time-of-Flight Mass Spectra

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United States Department of Agriculture

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Kim Prather

University of California, San Diego

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Relative Sensitivity Factors for Alkali Metal and Ammonium Cations in Single-Particle Aerosol Time-of-Flight Mass Spectra

Deborah S. Gross, Markus E. Gälli, Philip J. Silva, and Kimberly A. Prather*

Department of Chemistry, University of California, Riverside, California 92521

A variety of factors have been investigated with regard to the quantitation of chemical species within individual ambient aerosol particles analyzed by laser desorption time-of-flight mass spectrometry. Spectrum to spectrum differences in the interaction of the particle with the ionization laser beam, which affect the absolute peak areas in the mass spectra, can be minimized by using relative peak areas instead of absolute peak areas in each spectrum. Whereas absolute peak areas vary by an average of 59% for a given ion peak in single particle mass spectra of a monodisperse aerosol of particles formed from the same solution, relative peak areas in the same mass spectra vary only by an average of 16%. Relative sensitivity factors (RSF) relating the mass spectral ion intensity of NH_4^+ and the alkali metal cations Li^+, Na^+, K^+, Rb^+, and Cs^+ in single particle aerosol time-of-flight mass spectrometry to their bulk concentrations have been determined. The values for Li^+/Na^+, K^+/Na^+, Rb^+/Na^+, Cs^+/Na^+, and NH_4^+/Na^+ are found to be 0.14, 5.1, 6.0, 7.9, and 0.014, respectively. The higher response for heavier cations of the alkali metals is consistent with the periodic trends of both ionization potential and lattice energies of the species of interest. The response factor for sodium and potassium cations has been used to accurately determine the relative amounts of Na^+ and K^+ in sea-salt particles, by analyzing a sample of ∼360 ambient sea-salt particles. The relative amounts of Na^+ and K^+ are found to be 97 and 3% in particles, respectively, whereas in seawater they are, on average, 98 and 2%.

A critical goal of studies of atmospheric particulate matter involves source characterization, i.e. correlating the observed particles with the location from which they were emitted.[1−4] In addition, the reactivity and evolution of particle-associated chemicals can be investigated by comparing the chemical composition of single particles as a function of time and meteorological conditions, with geographical resolution. These results can be correlated with ambient gas-phase concentrations, to characterize heterogeneous reactions which occur in the troposphere.[5]

A number of research groups have developed instrumentation for on-line single particle mass spectrometry.[6−11] A comprehensive review of these techniques has been published by Wood and Prather.[12] Recent advances in aerosol time-of-flight mass spectrometry (ATOFMS) make it possible to obtain simultaneous mass spectra from both positive and negative ions in a single ambient aerosol particle, in real time.[13] The observed ions can be used as markers of the chemical species present in the particles, indicating either the origin of the particles, the subsequent chemistry which the particle has undergone, or both. For example, mass spectra of particles of marine origin typically contain large cation signals from Na^+ and K^+, as well as clusters of these cations with various anions such as Cl^-, NO_3^-, and SO_4^{2-}, species which are clearly indicative of sea salt. Not only do the peaks observed in the mass spectrum indicate the various chemical species present in the particle, but the relative intensities of the ions in the mass spectrum can provide quantitative information about the relative concentrations of these species in each particle.

A wide variety of analytical techniques rely on the use of relative sensitivity factors (RSF's) for obtaining quantitative or semiquantitative results from multicomponent samples, including mass spectral and separation methods. These factors correct for differences in the response of the various species to the method being used, as well as for changes in the response of a particular species due to changes in the sample matrix. These RSF's are empirically determined. Equation 1 shows the definition of the RSF in a situation where the species present are detected as ions, where n_i^X and n_a^X refer to the number of ions and atoms, respectively, of species X present in the sample.

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* To whom correspondence should be addressed.

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$$\text{RSF}\!\left(\frac{A}{B}\right) = \frac{n_i^{\text{A}}/n_i^{\text{B}}}{n_a^{\text{A}}/n_a^{\text{B}}} \qquad (1)$$

RSF's have been determined for a variety of ionic and metallic species in aerosol particles, using laser microprobe mass spectrometry (LMMS). Studies have focused on fly ash particles,[14,15] glasses and shards,[16] synthetic sea-salt analogues,[17] and doped metallic particles.[18] Questions were raised in each of these studies about the applicability of the determined RSF factors to unknown particles, because of variability in the RSF due to differences in the particle matrix.

In contrast to the off-line technique LMMS, the possibility of quantitation of species in particles measured in real time by laser-desorption mass spectrometry has been investigated by Wexler and co-workers.[19] Liquid glycerol droplets were formed containing varying concentrations of five test ions, Fe^{3+}, Na^+, Cl^-, NO_3^-, and SO_4^{2-}. The calibration curves of absolute peak areas of these ions versus solution concentration were linear over at least 2 orders of magnitude, corresponding to detection limits in the 10^{-2}–10^{-5} M range. Absolute peak areas of specific ions in identical droplets were found to vary by as much as 58% over the course of an hour, although no time dependence was observed.

To overcome scatter in the absolute peak areas of each ion in a sample of spectra of identical particles, Wexler and colleagues suggest averaging the mass spectra, for the resulting $N^{1/2}$ increase in the precision of the peak area measurement (where N is the number of spectra averaged). They later applied this methodology to binary solutions made of sodium, potassium, and ammonium salts, to study the crystallization processes.[20] However, application of this methodology to ambient particles, where the particle population can be a complex mixture of many different compositions depending on source[21,22] and individual particle composition information is desired, is not practical due to the variability in the particles. In this paper, we present an alternative method to address the variation in absolute peak area within a data set of many nonidentical particles.

Recently, Wexler and co-workers presented results for small particles (12–150 nm) showing a relative signal for K^+ 4.9 times that for Na^+, based on calculated ion yields from single component KCl and NaCl particles, respectively.[23] However, other results presented by this same group for small single component KCl and NaCl (12–150 nm) particles show this ratio reversed.[24] These

contradictory results highlight the need to gain a better understanding of the ionization process in mass spectrometry of single particles.

Quantitation of the species present in individual aerosol particles by laser desorption/ionization mass spectrometry requires a comparison of the number of ions formed when the particle interacts with the laser versus the number of neutral atoms of each species, as shown in eq 1. We make the approximation that the ratio of the number of atoms present will be equal to the ratio of atoms present in the bulk particle. The ion intensity ratio is directly measured from the mass spectrum. Thus, the RSF of any pair of ions can be directly determined from the slope of the ion intensity ratio plotted as a function of the ion ratio in solution, for multiple solution ratios.

Empirical RSF's are needed to obtain quantitative, or relative concentration, information about species in individual particles, because the ionization efficiency of the species in the particles depends on a variety of parameters which are not known explicitly. Factors such as the ionization potential of the species, the lattice energy of the specific salt analyzed, the absorption cross-section at the wavelength of the ionization laser used, and the interaction of the incident laser light with the particle can vary for each species and each particle. To obtain relative quantitation information for the ions observed in the mass spectrum of any ambient particle, it is necessary to have a measured relative sensitivity factor for each pair of cations or anions observed, in the appropriate matrix. This is a tremendous task, given the complexity of ambient particulate matter. A reasonable starting point, and one which will make comparisons between different on-line single particle techniques possible, is to begin with a variety of binary mixtures and to determine RSF's in simple systems. Results from simple systems can then be compared to the RSF's determined for the same ion pairs in more complex chemical matrices. Here we report RSF's for the cations of the alkali metals and NH_4^+ measured with ATOFMS. This study has the practical goal of helping us quantify the relative amounts of the various species in particles observed in ambient air. In addition, it can provide information about the ionization process occurring in the laser desorption of individually suspended particles. Several of these ions are detected frequently during ambient studies of particles using ATOFMS.[21] The Na^+/K^+ cation pair is of particular interest, since these ions are present in large abundance in particles of marine origin, which are often a significant percentage of the ambient particles observed throughout the Los Angeles air basin. We demonstrate the applicability of this RSF to "real-world" particles by calculating the relative concentrations of Na^+ and K^+ in the mass spectra of individual ambient sea-salt particles.

EXPERIMENTAL SECTION

Single-Particle Mass Spectra. Mass spectra were obtained using both laboratory based and transportable ATOFMS instruments which are described in detail elsewhere.[13,21] Briefly, aerosol particles are introduced into the vacuum system through a convergent nozzle and skimmers, which collimate the particle beam. The aerodynamic diameters of the particles are determined from their time-of-flight over a known distance between two orthogonal continuous wave argon ion laser beams. The start and stop times are determined by a timing/logic circuit, triggered by light scattered from the particles as they traverse the laser beams.

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Table 1. Concentrations of Ions in the Equimolar Solutions Used in This Study[a]

M^+	M^+/Na^+ (solution)	$[Na^+]$ (μM)	$[M^+]$ (μM)	mol of Na^+/particle ($\times 10^{-15}$ mol)	mol of M^+/particle ($\times 10^{-15}$ mol)
NH_4^+	1.0	56.5	57.9	4.66	4.66
Li^+	1.0	56.5	56.6	15.94	15.94
K^+	1.0	44.5	45.6	6.30	6.30
Rb^+	1.0	30.8	29.8	7.36	7.36
Cs^+	1.0	22.2	20.8	3.93	3.93

[a] The solutions are mixtures of only NaCl and a second chloride salt in 50/50 methanol/water (by volume). Also included is the average number of moles of each cation per single mode particle measured here.

When a particle crosses the second laser beam, the timing/logic circuit stops, reverses, and counts down, triggering a Nd:YAG laser (266 nm) to fire when the particle is in the center of the source region of the time-of-flight mass spectrometer. The laboratory based instrument is operated for a single ion polarity, whereas the transportable instrument has a dual collinear reflectron design, in which positive and negative ions are simultaneously accelerated down the two flight tubes. Typically, between 10 and 40% of the particles sized by ATOFMS are desorbed and ionized by the Nd: YAG laser, yielding mass spectra. These mass spectra are detected using microsphere plate (MSP) detectors in the transportable instrument, and with a microchannel plate (MCP) detector in the laboratory based instrument. Thus, both the velocity and chemical composition of each particle is obtained. The velocity can be converted to an aerodynamic size using an empirical calibration curve. Since cations were the focus of this study, only positive ion spectra were acquired in the experiments reported here.

Particle Generation. For this study, a monodisperse aerosol was generated using a vibrating orifice aerosol generator (VOAG) (TSI, Inc., St. Paul, MN). Salt solutions were made from NH_4Cl, NaCl, and KCl (Sigma Chemical Co., St. Louis, MO) and LiCl, RbCl, and CsCl (Aldrich Chemical Co., Milwaukee, WI) diluted in 50/50 methanol/water (by volume). Solution concentrations were chosen to generate particles with aerodynamic diameters of $\sim$0.8 μm, and are shown in Table 1, along with the average number of moles of each cation in the particle. In addition to these single $\sim$0.8 μm particles, larger particles were also formed by the VOAG, in which two and three particles coalesced (termed doublets and triplets, respectively). For the Na^+/K^+ ion pair, a range of solution concentrations was used in order to determine the linearity of the RSF; these are shown in Table 2. Ambient sea-salt particles were sampled directly from the ambient air and analyzed using a transportable ATOFMS instrument located in the laboratory in Riverside, CA. Sampling was carried out during a time period when the ambient air was characterized by a marine (Pacific Ocean) layer.

Data Analysis. Mass spectra were obtained from approximately 600 particles from each solution. The single particle mass spectra were then separated by particle size, so that singlet, doublet, and triplet particles were compared only to themselves. In addition, spectra in which any of the peaks due to atomic ions saturated the 8-bit data acquisition system were discarded, since the relative peak areas could not be determined accurately.

RESULTS AND DISCUSSION

Single-Particle Mass Spectra. It is evident from the mass spectra of particles formed from a solution containing known concentrations of different cations that the instrumental response to these cations is not identical, and thus RSF's are needed to better interpret the resulting spectra. Figure 1 shows single particle mass spectra of particles containing sodium and potassium, formed from solutions 2 and 8 (Table 2). Each spectrum results from a single laser shot interacting with a single particle. Evident in these spectra are peaks corresponding to Na^+ and K^+, as well as the cluster ions K_2Cl^+ and Na_2Cl^+, from solutions 2 and 8, respectively (see Table 2). These clusters, as well as mixed clusters such as $NaKCl^+$, were observed in a number of the particles formed from each of the solutions. No other ions were present in the mass spectra. Figure 2 shows single particle mass spectra of particles containing lithium and sodium, and rubidium and sodium, respectively (see Table 1). Clearly the ratio of the relative intensity of the cation signals does not directly reflect the solution concentration ratios in any of these cases. To obtain an RSF which can be used to determine the relative amounts of sodium and potassium in an ambient particle, we measured particles containing these ions over the widest possible range of salt concentrations. Solutions 1 and 8 have concentrations very near the detection limits for Na^+ and K^+, respectively, implying that the detection limits for these species are $\sim$0.45 $\times 10^{-15}$ and 0.03×10^{-15} mol, respectively, in the ATOFMS instrument.

Before acquiring spectra from which the ion intensity ratios could be reliably determined, the gain on the detectors used in both the transportable and laboratory ATOFMS instruments had to be decreased to $\sim10^5$, versus the gain of $\sim10^6$ typically used. Under normal operating conditions, the gain value is maximized to increase the percentage of sized particles from which mass spectra are also obtained, as well as to maximize the number of chemical species which are detected in each mass spectrum. However, under these conditions signals from Na^+ and K^+ cations routinely saturate the detector and/or the dynamic range of the data acquisition system, leading to clipped peaks and making it impossible to obtain quantitative peak areas. In addition to decreasing the detector gain, a 12 dB attenuator was placed between the detector anode and the data acquisition board on the transportable instrument. These two parameters were adjusted such that 600 mass spectra were acquired in a reasonable amount of time, and <10% of the spectra saturated the detector or the data acquisition system. The spectra which did saturate the detection system were discarded. As discussed by Wexler and co-workers,[19] the need to adjust these parameters in the data acquisition system will make it difficult to directly acquire mass spectra from unknown particles which can be quantitated. We are pursuing a variety of methods to improve the dynamic range of the data acquisition system, to overcome this limitation.

Reproducibility of Peak Areas. Useful RSF's can be obtained from single particle mass spectra only if the signal intensity is both reproducible and has relatively low scatter over a large sample of particles. Typically, the measured absolute peak areas vary widely for particles sampled from a monodisperse aerosol, presumably because of inhomogeneities in the laser beam (i.e. differences in power density in the beam cross-section), which lead to differences in the energy imparted to the particles during

Table 2. Concentrations of Na$^+$ and K$^+$ Ions in the Eight NaCl/KCl Solutions Used in This Study[a]

solution	Na$^+$/K$^+$ (solution)	[Na$^+$] (μM)	[K$^+$] (μM)	Na$^+$ peak area (absolute)	Na$^+$ peak area (relative)	K$^+$ peak area (absolute)	K$^+$ peak area (relative)
1	0.5	25.7	48.3	979 ± 1486	0.076 ± 0.092	12847 ± 14478	0.718 ± 0.113
2	1.0	38.5	36.9	1411 ± 833	0.152 ± 0.047	5544 ± 2252	0.688 ± 0.085
3	5.1	68.4	13.4	3138 ± 1519	0.448 ± 0.055	3091 ± 1371	0.453 ± 0.041
4	9.0	75.3	8.4	4287 ± 1711	0.541 ± 0.055	2799 ± 1242	0.346 ± 0.036
5	14.7	78.7	5.4	4321 ± 1775	0.589 ± 0.070	2168 ± 1048	0.283 ± 0.042
6	18.4	80.0	4.4	4372 ± 1703	0.663 ± 0.071	1539 ± 822	0.220 ± 0.048
7	30.5	81.8	2.7	3918 ± 1847	0.706 ± 0.073	905 ± 598	0.146 ± 0.040
8	38.6	82.8	2.2	4004 ± 1674	0.752 ± 0.067	580 ± 357	0.100 ± 0.030

[a] The solutions are mixtures of only NaCl and KCl, in 50/50 methanol/water (by volume). Average and standard deviations of absolute and relative peak areas of Na$^+$ and K$^+$ ions formed from the laser desorption of individual aerosol particles from these solutions are also shown.
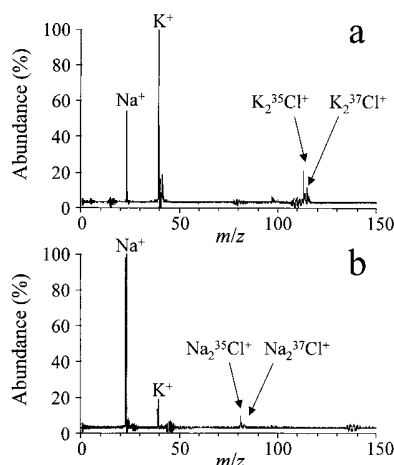

Figure 1. Time-of-flight mass spectra of individual NaCl/KCl particles formed from (a) solution 2 (Na$^+$/K$^+$ = 1.0) and (b) solution 8 (Na$^+$/K$^+$ = 38.6). Atomic ions as well as clusters with the Cl$^-$ counterion are labeled. Each spectrum is the result of a single laser shot interacting with a single particle.
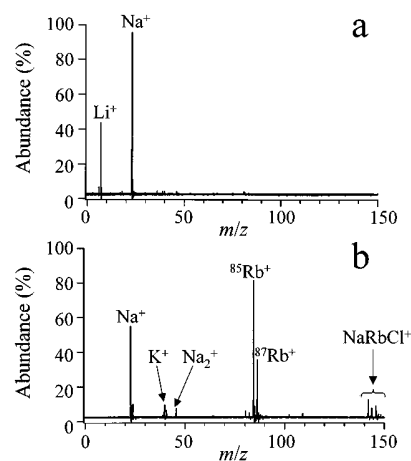

Figure 2. Time-of-flight mass spectra of individual particles formed from (a) a solution of LiCl and NaCl (Na$^+$/Li$^+$ = 1.0) and (b) a solution of NaCl and RbCl (Na$^+$/Rb$^+$ = 1.0). Atomic ions as well as clusters with the Cl$^-$ counterion are labeled. Each spectrum is the result of a single laser shot interacting with a single particle.

Figure 3. Scatter in the relative peak areas of Na$^+$ (♦) and K$^+$ (○) in the 414 single mode particles measured from solution 7 (Na$^+$/K$^+$ = 30.5). Horizontal lines indicate the average peak areas, 0.71 ± 0.07 and 0.15 ± 0.04 for Na$^+$ and K$^+$, respectively.

the ionization process. Standard deviations of the average absolute peak areas range from 39 to 152% for Na$^+$ and K$^+$, over a sample of 200−300 "identical" particles, for the solutions listed in Table 2. Standard deviations in peak area of this magnitude were also observed by Wexler and co-workers[19] and Bate et al.[18] from mass spectra of individual aerosol particles, examined on-line and by LMMS, respectively. However, the majority of the fluctuation in absolute peak areas depends only on the total area under all of the ion peaks in the mass spectrum, which increases if the ionization laser interacts with more of the particle and/or if a particle interacts with a higher energy spot in the laser beam. Currently these two factors cannot be separated. Therefore, examination of the relative peak areas, in which the area of each peak is normalized to the total area under all peaks in the spectrum, should be more reproducible. Figure 3 shows the measured relative peak areas for Na$^+$ and K$^+$ for all ∼0.8 μm particles from solution 7. The standard deviation of the average areas for each of these cations in most solutions drops to between 9 and 31%. [This value does not include the standard deviation of the relative area of Na$^+$ from solution 1, which is essentially at the detection limit for this cation, and has a standard deviation of 121%. Inclusion of this value increases the average standard deviation from 16 to 22%.] The variation is dramatically less than
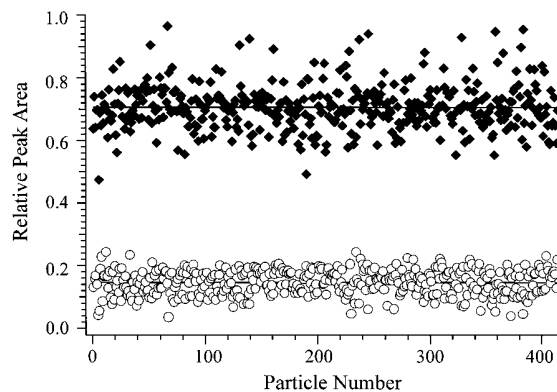
that in the absolute areas of the same peaks. Table 2 gives the average and standard deviation of the absolute and relative peak areas for the single mode particles measured. These results demonstrate that the relative peak areas determined from single particle mass spectra are directly comparable, *without* the need for averaging multiple spectra. A comparison of the ratio of the

relative area of any peaks within an individual spectrum to the ratio of the same peaks in another spectrum will provide relative quantitation to within ~10−20% and will be applicable to individual ambient particles, provided that the effect of the matrix of the ambient particle is understood (see below).

Determination of RSF's for Ion Pairs. RSF values for alkali metal cations as well as NH_4^+ were determined relative to Na^+ in the ATOFMS instrument. This initial set of ion pairs was chosen to provide a framework of useful ion pairs on which to build in future studies. In addition, RSF's for some of these species have been investigated using other techniques, giving us an opportunity to compare the response of the ATOFMS to other single particle instruments.

There are a number of factors which must be taken into account in order to obtain an accurate RSF for any ion pair which will be of practical application for analysis of the mass spectrum of an individual ambient particle. First, several ions which we have investigated in this study have multiple isotopes (Li^+, K^+, and Rb^+). For these ions, the most common isotope (m/z 7, 39, and 85, respectively) was used for comparison with the Na^+ (m/z 23) intensity. Observation of the less abundant isotope peaks in the spectrum of an ambient particle could be precluded by either spectral congestion or a low intensity of the metal cation peak. Second, high-intensity peaks in the ATOFMS spectra typically exhibit some "ringing", due to partially saturating the data acquisition system and/or signal reflections within the data acquisition circuitry, and this could mask low-intensity isotope peaks under certain circumstances. When this occurs, the peak area in a mass spectrum due to a particular ion is divided into multiple peaks. To calculate an accurate peak area in cases where this does occur, we use the sum of the relative area of all of the peaks ±0.5 Da of the most abundant isotope. Thus, the calculated relative sensitivity factors should be independent of peak ringing. Third, we have chosen to compare only the signal from the atomic cations, neglecting the signal from cluster ions. We chose this approach for a variety of reasons: the relative percentage of the signal in cluster ions is relatively constant in the solutions investigated, and most importantly, the eventual goal is to apply this RSF to mass spectra obtained from ambient particles. While the majority of peaks in a mass spectrum of an ambient particle should be identifiable, it is possible that high-mass cluster ions containing these cations could be formed and be difficult to identify. Thus, requiring that they be included will make quantitation more difficult. However, both of these assumptions will likely depend on the particle matrix.

The most accurate method for determining RSF values is to use a series of solutions containing the two ions of interest at differing concentration ratios. The RSF is determined from the measured relative intensities of the ions in each mass spectrum as a function of the ratio of their solution concentrations. This method was carried out for the K^+/Na^+ ion pair, as it is the most commonly seen ion pair of those investigated in this study. The series of solutions containing only KCl/NaCl listed in Table 2 was used for this purpose.

Figure 4 shows the relationship between the solution Na^+/K^+ concentration ratio and the ion ratio for each of the particle size modes, singlet, doublet, and triplet. For each solution, these data points are typically averages of ~250−400 singlet particles, ~150−
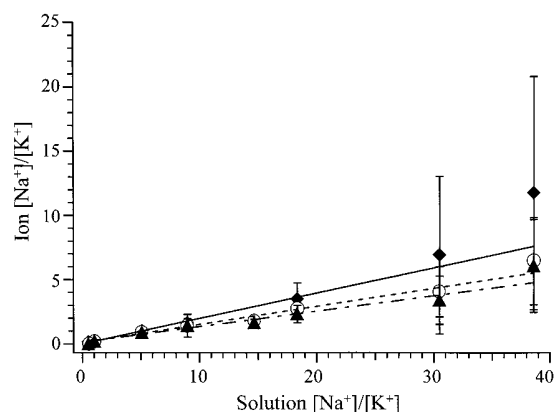

Figure 4. Ratio of ion intensities as a function of the ratio of solution concentrations of Na^+ and K^+, for single (◆), double (○), and triple (▲) mode particles. Included are the weighted linear least-squares fits to the data; the K^+/Na^+ RSF is obtained from the inverse of the slope of this line and is 5.1 for the single mode particles.

200 doublet particles, and ~50−100 triplet particles. Clearly, within the error bars there is no dependence on particle size over this relatively narrow size range. The large error bars associated with singlet particles from solutions 7 and 8 are likely due to the fact that we are approaching the detection limit for K^+ in these particles. Although the data set is smaller for the doublet and triplet particles, they contain more material, leading to somewhat less scatter in the peak areas and therefore smaller standard deviations. The K^+/Na^+ ratio as a function of the mole fraction of KCl in the original solution closely matches data published by Wexler and co-workers.[20]

In Figure 4, weighted least-squares fits to the data sets are also shown. [The points were weighted by the average of the ratio of the relative peak areas divided by the standard deviation. The linear least-squares fit was constrained to have an intercept of 0.] The RSF for potassium versus sodium is determined from the inverse of the slope of the line for the singlet particles and is found to be 5.1 for this cation pair for the ~0.8 μm particles. This is exactly the value obtained by measuring the ion signal ratio from the equimolar solution of NaCl/KCl. Our measured relative sensitivity factor differs from the value calculated from Van Grieken's results,[17] which suggest an RSF for K^+/Na^+ of 4.2, based on the RSF of each of these ions with respect to NH_4^+ (150 and 630, respectively). Considering differences in matrices, as well as in the ionization process, it is not surprising that the LMMS and ATOFMS numbers are not identical. The ionization processes in LMMS, in which a particle is immobilized on a surface and is desorbed and ionized by a laser beam, versus a suspended particle interacting with a laser beam are most likely different. Finally, laser energy used in LMMS is typically much lower (0.1−100 μJ)[25,26] than that used in ATOFMS. Our value of 5.1 is in better agreement with that found by Wexler and co-workers,[23] although their statement that the relative ion yield should increasingly favor Na^+ for larger KCl/NaCl particles is not borne out by our results. Wexler and co-workers point out that these differences may be

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Table 3. Relative Sensitivity Factors (RSF's) Relative to Na$^+$ Obtained for Alkali Metal and Ammonium Cations Using ATOFMS^a

M$^+$	[M$^+$]/[Na$^+$] (solution)	measured RSF (M$^+$/Na$^+$)	ionization potential (eV)	lattice energy (eV)
NH$_4^+$	1.0	0.014		
Li$^+$	1.0	0.14	5.39	834
Na$^+$	1.0	1.0	5.14	769
K$^+$	1.0	5.1	4.34	701
Rb$^+$	1.0	6.0	4.18	680
Cs$^+$	1.0	7.9	3.89	657

^{a} Particles were generated using the solutions listed in Table 1. Ionization potentials and lattice energies are from ref 27.
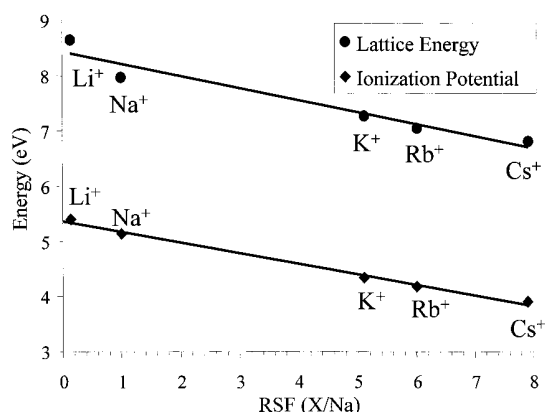

Figure 5. Graph of relative sensitivity factor (M$^+$/Na$^+$) versus lattice energy of the chloride salt (●) and first ionization potential of the element (♦), in electronvolts (eV).

attributable to differences in the ionization laser wavelength used, rather than the particle size. This further highlights the fact that the measured RSF values are not necessarily the same in slightly different instrumental setups, as well as the need to generate sets of RSF values which can be used to analyze mass spectra acquired with specific single particle techniques, as we are doing here.

Because of the linear response of relative ion intensity to relative solution concentrations for the K$^+$/Na$^+$ cation pair over the entire dynamic range of our instrument, it appears that the RSF's can be obtained by the measurement of the ion response for only one solution. However, the large scatter in the relative intensities of each cation at concentrations approaching their respective detection limits indicates that this could introduce additional error in the measurement. This error will be minimized by using a solution concentration that gives roughly equal ion signal from each ion. Assuming that the composition of the particles is representative of the composition of the solution from which they were formed, a direct measurement of the relative ion intensity of two ions from a solution containing equal concentrations gives the relative ion response as shown in eq 1.

Table 3 shows the RSF obtained from an equimolar solution, relative to Na$^+$, of each ion investigated here. For the alkali metal cations, a clear trend is observed in that the ATOFMS shows a greater response to the heavier elements that the lighter ones. This trend is shown graphically in Figure 5, where the RSF's are plotted as a function of the ionization potential[27] of each neutral

atom. Also plotted is the set of RSF's as a function of the lattice energy[27] of each chloride salt. Both plots demonstrate a strong linear relationship, with correlation coefficients (r^2) of 0.99 and 0.94, respectively. Both the lattice energy and ionization potential depend on the atomic/ionic radii of the ions considered; thus it is not surprising there is a linear relationship between the RSF and both parameters. Using these data, one cannot make any conclusions regarding the physical process occurring in the ionization mechanisms of species from these particles. Current theories about ion formation in laser desorption are still in dispute.[28–31] From previous studies, it is unclear whether this involves a multiphoton ionization processes (MPI), in which case the ionization potential of the species is the important factor or the result of direct emission of ions from the solid phase of the lattice. Our results seem to be qualitatively independent of laser energy used, since the laboratory based ATOFMS has a significantly higher laser energy ($\sim$30 mJ) than the field transportable version ($\sim$1 mJ). Future work will include measuring these ratios as a function of laser power as well as varying the sample matrix. Changes in the RSF values under these varying conditions will help to elucidate the critical factor in the ionization process.

It is obvious from the results shown in Table 3 that ATOFMS is much more sensitive to all of the alkali metal cations than to the ammonium ion. Our measured RSF for the Na$^+$/NH$_4^+$ ion pair is 71 (a value of 0.014 for NH$_4^+$/Na$^+$). This differs from the measured value published by Van Grieken[17] who reports an RSF for Na$^+$/NH$_4^+$ of 150. Differences in these values are likely due to a variety of factors, most obviously that the particles measured by Van Grieken contained three cations, NH$_4^+$, Na$^+$, and K$^+$, and therefore possess a different matrix. Van Grieken and co-workers determined the response of various cations in a mixed particle containing ions commonly found in sea-salt particles: NH$_4^+$, Na$^+$, Mg$^+$, Al$^+$, K$^+$, Ca$^+$, and Fe$^+$. The RSF's, with respect to NH$_4^+$, were found to be 1, 185, 10.3, 16.8, 660, 12.8, and 12.1, respectively. This implies a RSF for K$^+$/Na$^+$ of 3.6 in this matrix, compared to 4.2 in a three-component particle. Thus, the RSF's of Na$^+$ and K$^+$, relative to NH$_4^+$, change by 23 and 5%, respectively, as the particle matrix is changed. Other LMMS studies have shown dramatic and varied matrix effects, with quantitation possible only within a factor of 5,[14] or within less than 50% relative standard deviation.[15] Clearly, variation of ion signal response as a function of particle composition, or matrix, has the potential to affect the applicability of our measured RSF values.

Application to Ambient Sea-Salt Particles. To investigate whether the relative sensitivity factor determined for Na$^+$/K$^+$ in laboratory generated particles is useful when applied to spectra of ambient particles, we calculated the relative concentrations of Na$^+$ and K$^+$ in seawater from the ion signal obtained in a set of single particle spectra of ambient sea-salt particles. The spectra of $\sim$360 individual particles, acquired over an approximately 20 h (8 pm through the following afternoon) period in Riverside, CA,

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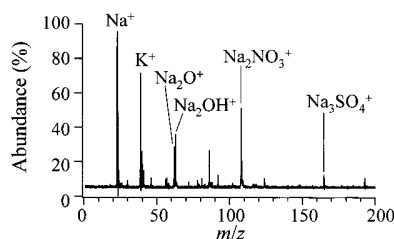
Figure 6. Ambient sea-salt particle collected in Riverside, CA. The detector gain was decreased and the signal was attenuated in this spectrum, to keep all of the peaks on scale.

were examined. These particles were selected on the basis of their chemical composition from the ~8000 ambient particles which were sampled during this time period, and only those in which the signal from all of the peaks was on-scale were used. See Figure 6 for an example of the mass spectrum of one of these particles. The data were acquired under conditions similar to those used to determine the RSF value for K^+/Na^+, described above: the detector gain was decreased and the detector signal was attenuated. Although seawater is not a binary NaCl/KCl mixture, it may be reasonably approximated as such. The most common anion in seawater, Cl^-, is 6 times more concentrated than the second most common anion, SO_4^- (average concentrations of 0.54 M and 8.85×10^{-2} M, respectively).[27] Therefore, the seawater anion matrix can be reasonably approximated by Cl^-, as used in the RSF determination described above.

To test this assumption, the relative intensities of sodium and potassium in the spectra were then determined by combining the relative areas of the atomic cation and cluster ions. [There were no mixed cluster peaks such as $NaKCl^+$, which have signal due to both potassium and sodium cations, in these spectra. However, the relative contribution of each cation in such a mixed cluster ion could be determined by using the measured RSF.] We examined Na^+ and K^+ relative to the sum of Na^+ and K^+ signal only, not taking into account any other species also present. The signal due to sodium in each particle was multiplied by the RSF determined above, and the cation signal due to sodium and potassium in the entire data set was determined. Sodium accounted for 97% of the combined signal, and potassium, for 3%. The average molar ratios of sodium and potassium in seawater are 98 and 2%, respectively.[27] These values are remarkably similar, particularly given that the sea-salt particle matrix differs from the test particles from which the RSF value was determined, and that the values we are comparing to are the average seawater composition, which may differ from that of the particles sampled. As the matrix of the laboratory generated aerosols becomes more complex and more closely resembles that of sea-salt particles, these numbers should become even more similar.

This result suggests that measured RSF's can be used for meaningful quantitation of aerosol mass spectra, to within ~70% (our observed ratio of Na^+ to K^+ varies by this amount from the average value in seawater), even if the sample matrix is not identical to that of the standard particles from which the RSF was obtained. As mentioned above, we are investigating the effect of the matrix on the measured RSF further.

CONCLUSIONS

The results presented here demonstrate that individual single-particle mass spectra can provide us with information about the relative quantities of different ions in a single particle. In addition, the relative ion response of the alkali metals and ammonium is directly related to their bulk concentrations. These results are largely independent of particle size, within the size range studied here. A dramatic improvement in the reproducibility of peak areas, which is necessary for reliable quantitation, is demonstrated when areas are normalized to the total intensity of the mass spectrum. This gain results from such factors as the particle−laser beam interaction and laser shot-to-shot power variations being normalized out and obviates the need for averaging multiple mass spectra, which is not desirable when analyzing chemically unique ambient particles.

These measurements of single particle RSF's for these ion pairs using ATOFMS are the first in what will be a long series of experiments to obtain RSF's for ions which we commonly observe in mass spectra of ambient particles. Clearly, extension to complex matrices including organic species is necessary. With the framework provided by this study, we can now begin to determine the effects of more complex matrices on relative ion formation. Application to ambient sea-salt particles has shown that the K^+/Na^+ RSF is useful for calculation of actual bulk concentration ratios of particle-associated chemical species. The use of a more complete set of these RSF's will make quantitation of the concentrations of species in individual ambient aerosol particles possible from their mass spectra. This will be of tremendous use when investigating the sources as well as the heterogeneous chemistry of ambient particles.