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## In Situ Measurement of the Aerosol Size Distribution in Stratospheric Solid Rocket Motor Exhaust Plumes

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**Abstract.** The concentration and size distribution of aerosol in the stratospheric exhaust plumes of two Space Shuttle rockets and one Titan IV rocket were measured using a two component aerosol sampling system carried aboard a WB-57F aircraft. Aerosol size distribution in the 0.01  $\mu\text{m}$  to 4  $\mu\text{m}$  diameter size range was measured using a two component sampling system. The measured distributions display a trimodal form with modes near 0.005  $\mu\text{m}$ , 0.09  $\mu\text{m}$ , and 2.03  $\mu\text{m}$  and are used to infer the relative mass fractionation among the three modes. While the smallest mode has been estimated to contain as much as 10% of the total mass of SRM exhaust alumina, we find show that the smallest mode contains less than 0.05% of the alumina mass. This fraction is so small so as to significantly reduce the likelihood that heterogeneous reactions on the SRM alumina surfaces could produce a significant global impact on stratospheric chemistry.

### Introduction

The global, steady state effect of chlorine loading from solid rocket motor (SRM) emissions has been modeled by several groups [Jones, 1995; Jackman et al., 1998]. These models typically predict that the annual average global total ozone (AAGTO) will decrease by about 0.03% as a result of present day space launch traffic (frequently taken as 726 tons of chlorine, the equivalent of nine Space Shuttle and three Titan IV launches).

Assessment of the global effects of SRM alumina particulate on stratospheric chemistry remain more uncertain. Modeling efforts are complicated by the requirement to account for the surface chemistry, size distribution, global transport, and sedimentation of the alumina. Until recently, there has been little data on which to base such a model. Molina et al. [1997] measured the rate of the chlorine activation reaction  $\text{ClONO}_2 + \text{HCl} \rightarrow \text{HNO}_3 + \text{Cl}_2$  on alumina surface and noted that the reaction was fast enough so as to raise the possibility that AAGTO might be reduced by chlorine activation on SRM alumina surface as much, or more than, the reduction from SRM chlorine loading alone.

Jackman et al. [1998] coupled the Goddard Space Flight Center two-dimensional photochemistry and transport model, the chlorine activation rates reported by Molina et al. [1997], and various models of the size distribution of alumina to

estimate the global impact of chlorine activation on alumina. They found that the magnitude of ozone loss from the chlorine activation is critically determined by the details of the assumed alumina size distribution. Adopting a trimodal size distribution of the type reported by Brady and Martin [1995], Jackman et al. [1998] demonstrated that the relative importance of the mechanism is dependent on the relative mass fractionation among the three modes. This result comes about because the rate at which alumina particles are removed from the stratosphere varies according to size and only the smallest mode of the alumina distribution remains in the stratosphere long enough to influence the stratosphere globally. Jackman et al. [1998] show that if about 10% of the alumina mass resides in the smallest mode, then the decrease in AAGTO associated with chlorine activation will be comparable to the decrease associated with SRM chlorine loading alone. The crucial parameter, then, required to reliably assess the impact of heterogeneous reactions on alumina from SRM exhaust appears to be the fraction of alumina mass residing in the smallest mode of the size distribution, particles with diameters near 0.01  $\mu\text{m}$ .

In this report, we present the first in situ measurement of aerosol size distribution in the stratospheric exhaust plumes of large SRMs covering a size range sufficient to infer a reliable estimate of the alumina mass fractionation. We compare the measured size distributions and mass fractionation to the previous work and apply the results to resolve some of the uncertainty assessing the global impact of SRM exhaust alumina on stratospheric ozone.

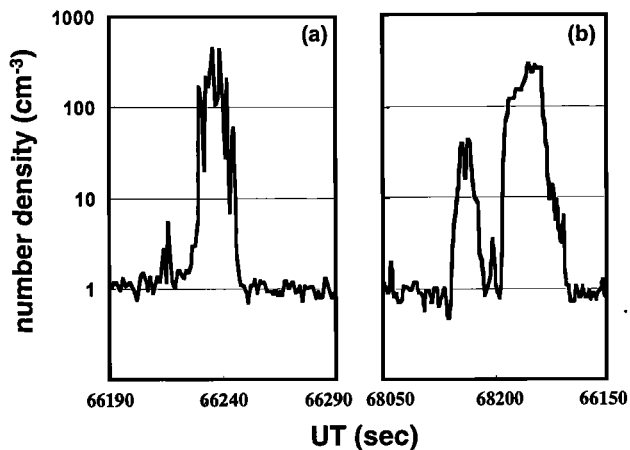
### Plume Measurement

Space Shuttle and Titan IV exhaust plumes were sampled on December 20, 1996 (T-IV), April 4, 1997 (STS-83), and August 8, 1997 (STS-85) from a WB-57F aircraft flying between 17 km and 19.5 km altitude. All data were obtained during plume encounters occurring between 5 minutes and 125 minutes after launch. Details of the WB-57F rocket plume wake sampling methodology and typical aircraft operations have been reported previously [Ross et al., 1997a, 1997b].

The measurements were made with an aerosol sampling instrument consisting of two subsystems: (1) a real time particulate counter (RPM) providing concentration and size distribution in a window covering 0.34 to 4  $\mu\text{m}$  at 1 Hz sampling rate and (2) a grab-tank sampling system (GTS) providing particulate size distribution in a window covering 0.01 to 0.4  $\mu\text{m}$ . The two instruments were carried in the WB-57F main payload bay. Independent, unheated, sampling

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**Figure 1.** Total aerosol concentration in the  $0.38 \mu\text{m}$  to  $4 \mu\text{m}$  size range as measured by the RPM for (a) encounter 3 and (b) encounter 12 of the Titan-IV plume on December 20, 1996. The average plume concentrations for (a) and (b) are  $162 \text{ cm}^{-3}$  and  $91 \text{ cm}^{-3}$ , respectively. The size distribution corresponding to encounter (a) appears in Figure 2 (c) as  $\blacktriangle$ .

inlets (6.35 mm and 9.53 mm diameter for the RPM and GTS, respectively) extended into, and were parallel to, the airflow outside the aircraft boundary layer. The RPM is based on a commercial laser particle counter, adapted for stratospheric plume measurements. Figure 1 presents RPM profiles of total concentration obtained during two encounters of the T-IV plume, illustrating the considerable structure in rocket exhaust plumes also noted by Ross et al. [1997a]. The profiles also serve as sensitive indicators of plume entrance and exit and serve to synchronize data sets from other instruments carried by the WB-57F. The RPM aerosol concentration outside of the plumes in clear stratospheric air, about  $1 \text{ cm}^{-3}$ , is consistent with other measurements of the stratospheric background concentration and size distribution [Fahey et al., 1995; Jonsson et al., 1995].

The GTS was chosen as the primary method for measuring the aerosol size distribution for sizes from  $0.01$  to  $0.4 \mu\text{m}$  because of the relatively brief duration of the rocket plume wake encounters. Submicron aerosols are typically characterized using condensation nuclei (CN) counting techniques and differential mobility analysis (DMA), which can require a stable sample source for up to 120 seconds. Typical plume encounters are only tens of seconds in duration, however, precluding the possibility of a real time DMA characterization. GTS samples were acquired by serially filling nine evacuated pressure vessels on command from the WB-57F aircrew based on a cockpit display of RPM data to indicate plume entrance. Each tank was then pressurized to one atmosphere with particle-free dry air to minimize modification of the sample by diffusion and agglomeration losses, then sealed. For particulate in the size range and concentrations of interest ( $< 10^3 \text{ cm}^{-3}$ ) the GTS post-acquisition sample modification can be estimated using the MAEROS model [Gelbard, 1983] that describes the evolution of an aerosol size spectrum. In this case, loss to the tank walls from Brownian motion causes the most significant change to the aerosol size spectrum with a predicted reduction in concentration by factors of 4, 0.4, and 0.1 at  $0.01$ ,  $0.02$ , and  $0.04 \mu\text{m}$ , respectively, over a three hour period. Shortly ( $< 60$  minutes) after aircraft landing, the GTS tanks were purged for

DMA analysis using the University of Missouri Mobile Aerosol Sampling System (MASS) to determine sample size distributions. [Hagen et al., 1993; 1998].

We note that the GTS tanks were contained in the unheated aircraft fuselage payload bay so that plume samples obtained at ambient temperature,  $\sim 220^\circ \text{K}$ , were gradually warmed during aircraft descent to a temperature greater than  $285^\circ \text{K}$ . Any condensed volatile component of the plume aerosol in the tanks would therefore have evaporated before it could have been sized by MASS. The net effect is that GTS data, even though the inlet was unheated, mimics data collected with a heated inlet. In contrast, RPM data would include a contribution from condensed volatile components of the plume aerosol.

## Results and Discussion

Figures 2 (a-c) show the measured particle size distributions as differential concentration versus diameter for the STS-83, STS-85, and T-IV exhaust plumes, respectively. Several things are apparent. First, the measured distributions are remarkably similar between the STS and the T-IV plumes. This is not surprising, given the similar size and performance characteristics of the SRMs of the two vehicles. Second, the GTS and RPM data sets are consistent in that they provide similar results near  $0.4 \mu\text{m}$ , where the measurement windows overlap. This consistency lends confidence that the GTS and RPM, operating on different physical principals, were performing satisfactorily and that the measured distributions over the entire window are reliable. This consistency also suggests that the plumes did not contain a significant condensed volatile component, at least near  $0.4 \mu\text{m}$ , since the RPM data reflect unheated sampling whereas the GTS samples were, in effect, heated. Third, the trimodal distribution is clearly evident, reaching maxima near  $2 \mu\text{m}$  and  $0.1 \mu\text{m}$  with a third maximum at or below the lower limit of the GTS measurement window,  $0.01 \mu\text{m}$ .

We model the measured size distributions by fitting the data to a trimodal Gaussian distribution of the type:

$$N(x) = \sum A_i \exp[-(x-X_i)^2 / \omega_i^2] \quad (1)$$

where  $x$  is the particle diameter and the fitting parameters  $A_i$ ,  $X_i$ , and  $\omega_i$  are adjusted to provide a least squares fit to the data. The derived parameters are then used to calculate the percentage mass fraction  $F_i$  in each mode under the assumption of constant particulate density across the entire size range. Table 1 presents the modal parameters  $A_i$ ,  $X_i$ , and  $\omega_i$  and associated uncertainties for the combined STS and T-IV data. The diameter of the smallest  $X_i$  mode is a special case. Figure 2 indicates that the actual size of this mode is equal to or less than  $0.01 \mu\text{m}$ . We know that  $X_i$  must exceed the size of a single  $\text{Al}_2\text{O}_3$  unit cell, about  $0.001 \mu\text{m}$  [Hsu and Kim, 1991]; thus  $X_i$  must fall in the range  $0.001 \mu\text{m} < X_i < 0.01 \mu\text{m}$ . It is reasonable to assume a value of  $0.005 \mu\text{m}$  for  $X_i$  in order to determine the remaining parameters in (1). Other choices for  $X_i$  in the appropriate range do not significantly affect our results. The mode sizes reported here,  $0.005$ ,  $0.09$ , and  $2.03 \mu\text{m}$ , agree somewhat with the mode sizes reported by Brady and Martin [1995],  $0.02$ ,  $0.28$ ,  $1.12 \mu\text{m}$  and Beiting [1997],  $0.06$ ,  $1.0$ , and  $3.6 \mu\text{m}$ . Caution must be taken in these comparisons, however, as the different models are based on different functional representations of the three modes. Beiting [1997], for example, reports mode sizes in terms of Sauter mean diameters in order to facilitate calculation of optical properties.

Table 1 also shows the percentage mass fractions  $F_1$  in the three modes derived from our measurements as 0.0008%, 0.22%, and 99.8%, smallest to largest. For comparison, the "best simulation" alumina model adopted by Jackman et al.

[1998], based on Brady and Martin [1995], places 12%, 8%, and 80% of the mass in the three modes. Beiting [1997] reported 1.2%, 1.5%, and 97.4 % of the mass in the three modes.

The critical parameter with regard to the consequences of heterogeneous reactions on SRM alumina surface is the relative mass residing in the smallest mode,  $F_1$ . The results of [Jackman et al., 1998] show that the steady state percent change in AAGTO ( $\Delta$ ) from chlorine activation on SRM alumina surface from present day launch vehicle traffic emission can be approximately expressed as

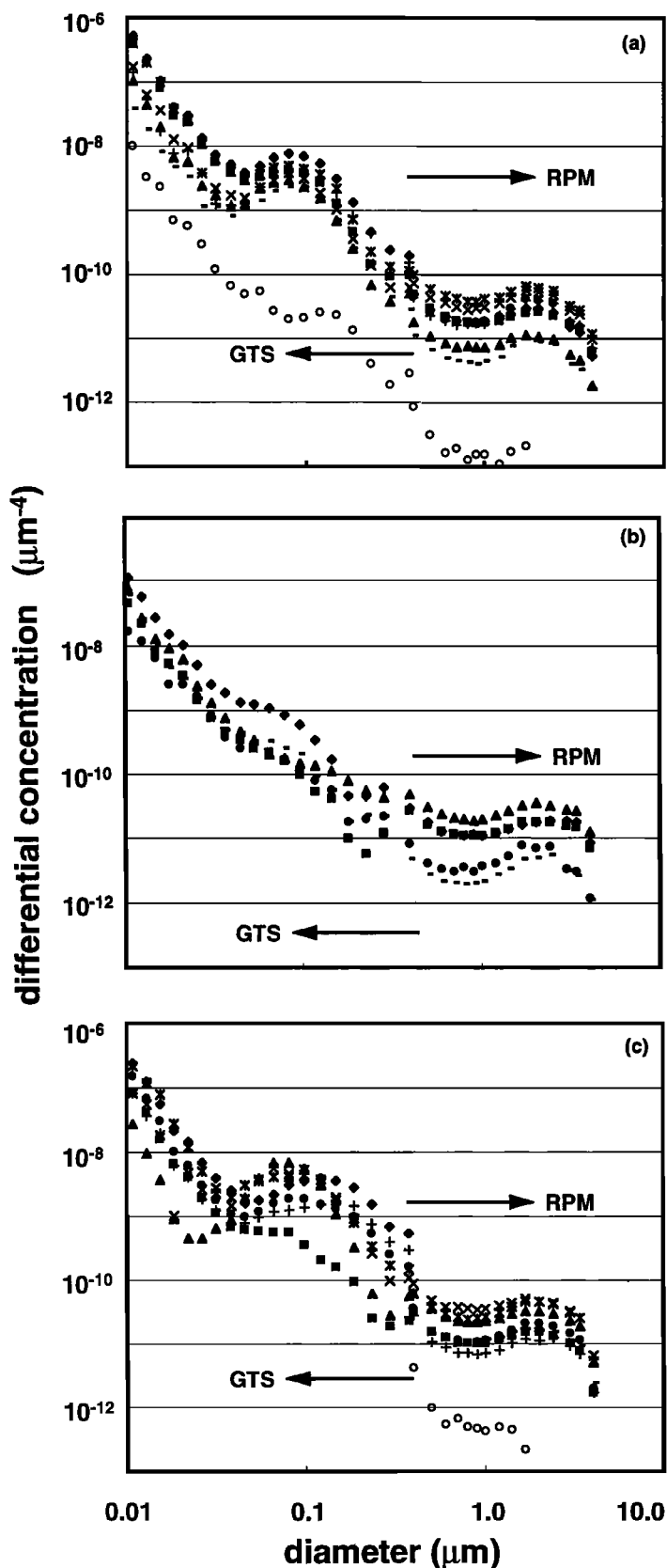
$$\Delta(\%) = -0.0009 F_1(\%) \quad (2)$$

Jackman et al.'s [1998] choice of  $F_1$  equal to 12% corresponds to a loss in AAGTO of about 0.01%, just under one half of the estimated loss to due the chlorine emission from the SRMs alone. Using our measured  $F_1$ , the AAGTO decrease is only about  $7 \times 10^{-7} \%$ . This result has far reaching implications for assessing the environmental impact of SRM emissions. Our measurement based  $F_1$  implies that so little SRM alumina remains in the stratosphere for a sufficiently long period of time that it can not be considered to represent a significant route to stratospheric ozone loss, at least insofar as the reaction  $\text{ClONO}_2 + \text{HCl} \rightarrow \text{HNO}_3 + \text{Cl}_2$  is concerned.

Indeed,  $F_1$  appears to be so small that the argument can reasonably be generalized so as to include any plausible heterogeneous reaction on the alumina surface. Even for some hypothetical reaction probability 1.0 on alumina surface, for example, it is difficult to construct any reaction series that could significantly influence stratospheric composition if our results and Jackman et al.'s [1998] conclusions that lead to (2) are correct. A more complete representation of alumina vertical transport in the stratosphere is required to verify the model predictions that lead to (2) and fully resolve the issue.

There is some uncertainty in the RPM data related to inlet enhancement due to inertial effects that could influence the differential size distribution in the largest mode and, therefore, the percentage mass fractions  $F_1$  for all modes. Lacking a complete description of these effects, it is instructive to examine how an upper limit could influence  $F_1$ . Under the most extreme correction factor, (the ratio of the aircraft velocity to the velocity of air in the sample inlet [Rader and Marple, 1986]),  $F_1$  would be increased by a factor about 60 to about 0.05%. Even this value is an order of magnitude less than Beiting [1997] and two orders of magnitude less than the  $F_1$  assumed by Jackman et al [1998] as a "best estimate", leaving the main thrust of our conclusion unchanged.

The origins of the discrepancies among our results, Brady and Martin [1995], and Beiting [1997] are not clear but may be related to the fact that the previous work combined data from



**Figure 2.** Size distributions measured in-situ for the STS-83 and STS-85 Space Shuttle plumes and the K-13 Titan-IV plume in (a), (b), and (c), respectively. The symbols  $\diamond$ ,  $\square$ ,  $\triangle$ ,  $\times$ ,  $*$ ,  $\bullet$ ,  $+$ ,  $-$ , and  $\circ$ , refer to data obtained during plume encounters 1 through 8 and clear air background obtained between encounters 4 and 5, respectively. (The STS-85 mission did not obtain a suitable background measurement.) Encounters began about 5 minutes after launch with approximately 6 to 10 minutes between successive encounters and between 17.8 and 19.3 kilometers altitude.

**Table 1.** Derived Model Parameters for Alumina Size Distribution

	Mode		
	1	2	3
$X_i$ ( $\mu\text{m}$ )	0.005	$0.090 \pm 0.008$	$2.03 \pm 0.05$
$A_i$ $10^{-11}$ ( $\mu\text{m}^{-4}$ )	$38330 \pm 10100$	$254 \pm 93.2$	$2.52 \pm 0.48$
$\omega_i$ ( $\mu\text{m}$ )	$0.006 \pm 0.0006$	$0.090 \pm 0.015$	$1.49 \pm 0.045$
$F_i$ (%)	$0.0008 \pm 0.00014$	$0.22 \pm 0.16$	$99.8 \pm 0.06$

different experiments (Cofer et al. [1991]; Strand et al. [1981]; Zolensky et al. [1989]) that sampled particulate in different atmospheric regions, covering different, limited, portions of the size range of interest. If the physical characteristics of SRM exhaust alumina vary with altitude, for example, data obtained in the troposphere may not be reasonably combined with data obtained in the stratosphere to generate a comprehensive model. Given the importance of an accurate determination of the  $F_i$  with respect to assessing stratospheric impacts, corroborating stratospheric measurements and further modeling are suggested in order to confirm our results and firmly resolve the discrepancies.

## Summary

We report the first in situ measurement of the size distribution of  $0.01 \mu\text{m}$  to  $4 \mu\text{m}$  alumina particulate emitted by large solid fueled rocket motors into the lower stratosphere. Our measurements generally agree with previous reports insofar as we find that the alumina assumes a trimodal distribution. Our measurements significantly disagree with previous efforts to describe the relative mass fractionation among the three modes, however. In contrast to previous models of the size distribution suggesting that between 1% and 10% of the total mass of emitted alumina resides in the smallest mode, our measurements show that less than 0.05% resides in the smallest mode. The reason for the disagreement is not clear but may be related to the fact that previous work was based on a synthesis of data obtained from different experiments and under different conditions. Our conclusion that less than a few hundredths of a percent of the alumina mass resides in the smallest mode, coupled with results from a recent model of the global impact of chlorine activation on alumina surfaces, indicates that heterogeneous reactions on alumina emitted by SRMs have only insignificant influence on stratospheric chemistry, in absolute terms and in comparison to the chlorine emitted by SRMs. Finally, the critical nature of the alumina size distribution with respect to accurately assessing the environmental effects of rocket emissions suggests that further measurements in SRM plumes should be carried out to confirm our results.

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