AIAA 80-0354R

Characterization of Particulates in the Exhaust Plume of Large Solid-Propellant Rockets

Leon D. Strand,* James M. Bowyer,† Guilio Varsi,‡ Eric G. Laue,§ and Robert Gauldin¶
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif.

Because of the very large size of the solid-propellant booster rockets employed by the Space Shuttle Launch System, and because of the projected high frequency of Space Shuttle launches, it has been necessary to estimate the effect of this launch activity on the environment. Two major combustion products of the rocket propellant employed in the Space Shuttle boosters are aluminum oxide (Al_2O_3) particles and hydrogen chloride (HCl) gas. This report is concerned with the characterization of these Al_2O_3 particles in the atmosphere. Size distribution and number density results obtained by flying aerosol collecting and analyzing instruments through the "ground clouds" and the high-altitude "exhaust plumes" generated by several Titan III launch vehicles, and by subsequent reduction of these data, are presented. The very-high-number densities of submicron-size particles detected in both the "ground cloud" and the high-altitude "exhaust plume" constitute the principal and, to some extent, unanticipated results of this investigation. Preliminary results regarding the physical appearance, chemical composition, and crystallography of the particles were obtained through examination of collected particulates by scanning electron microscopy.

Nomenclature

D_p = particle diameter
$\bar{D}_{pc}$ = mean particle diameter in size class, c
N_p = total number of particles in a given sample
N_{pc} = number of particles in size class, c
ΔN_{pc} = increment of particle number in size class, c
r = particle radius
T = Titan III launch time
α = diameter exponent in particle size distribution function
η = impactor-stage collection efficiency

Introduction

THE Space Shuttle booster consists of two very large solid rocket motors (SRMs), which together contain slightly more than 1000 metric tons of propellant. A major constituent of the exhaust ejected by these motors will be aluminum oxide (Al_2O_3) in particulate form (Table 1).

The size distribution of these particles is important with respect to 1) the light scattered by the particles while they remain suspended in the atmosphere, 2) the rates at which the particles will disperse into and will then be removed from the atmosphere, 3) the possible effects of these particulates on the pulmonary systems of man and animals, and 4) the possible participation of these particles in chemicophysical processes with other constituents of the exhaust plume.

Characterization of the size distribution of the Al_2O_3 particulates emitted by the Space Shuttle booster SRMs was the principal objective of the study reported here.

Extrapolation of the particulate data obtained from small SRMs to SRMs of the size employed by the Space Shuttle was known to be an unreliable technique at the time this study was conceived.[1-3] On the other hand, the SRM size, design, propellant characteristics, and internal ballistics, and the trajectories of the Space Shuttle were known to be similar to those of the Titan IIIC launch vehicle booster system. (The propellant mass contained in a Titan IIIC SRM is about 40% of that contained in a Space Shuttle SRM.)

In view of these anticipated physical and operational similarities of the Space Shuttle and Titan IIIC SRMs, a study program to monitor the exhaust products generated by Titan IIIC firings at the Eastern Test Range (ETR) and Western Test Range (WTR) and, in particular, to characterize the solid particulates emitted was initiated in late 1972.

Particulates were sampled in the vicinity of each of two parts of the Titan IIIC trajectory, viz., in the neighborhood of the launch site, from a few hundred meters to about 1 km, and at about 20-km altitude. The sampling instruments were installed in a UH1N helicopter in the case of the ground-cloud survey and in a U-2 airplane in the case of the high-altitude exhaust plume survey.

Test Equipment

A variety of sampling methods, including a quartz-crystal mass monitor, Nuclepore filters, sticky-tape impactors, a photoelectric cloud detector, and electrical mobility analyzers, were used to measure particulate concentrations and size distributions. A gaseous "grab sampler" was employed in early attempts to determine the chemical composition of gases and vapors within the ground cloud that was generated by the SRM exhausts. The most significant data were obtained from the sticky-tape impactors and from the electrical mobility analyzers; limited semiquantitative data were obtained from the Nuclepore filters.

Table 2 presents a summary of the experimental effort, together with an indication of those measurements that were successful and those that were unsuccessful, and a final summary of successful measurements.

The single-channel and multiple-channel sticky-tape impactors (designated SCI and MCI, respectively), together with the electrical mobility analyzers (EMAs), provided an in-

Table 1 Selected Shuttle exhaust products (metric tons)

Altitude	Al_2O_3	H_2O	HCl
First 1000 m	56	18	39
At 10 km, per 1000 m	6	2	4
At 20 km, per 1000 m	5	1.5	3.5
At 40 km, per 1000 m	1.5	0.5	1

Presented as Paper 80-0354 at the AIAA 18th Aerospace Sciences Meeting, Pasadena, Calif., Jan. 14-16, 1980; submitted Feb. 26, 1980; revision received April 6, 1981.

*Member of Technical Staff, Energy & Materials Research Section. Associate Fellow AIAA.
†Member of Technical Staff, Solar Energy Conversion Systems Section. Associate Fellow AIAA.
‡Manager, Chemical and Biological Processes Section.
§Member of the Technical Staff, Instrumentation Section.
¶Senior Engineer, Chemical and Biological Processes Section.

Table 2 Summary of measurements of Titan IIIC rocket emissions

Test data	Test location	Sampling instrumentation	
		Low-altitude	High-altitude
7-13-73	WTR	Quartz-crystal mass monitor[a] Evacuated-flask exhaust cloud sampler (EFS)[a]	
11-10-73	WTR	EFS SCI Photoelectric cloud detector	
4-10-74	WTR		Camera Nuclepore filter (NF) (90 mm)
10-29-74	WTR	SCI NF[a] EMA[a]	Multiple 2.5-cm Nuclepore filters (MNF)
5-20-75	ETR		MNF[a] MCI EMA
6-8-75	WTR	SCI NF EMA	MNF[a] MCI EMA
Summary of successful measurements		1 NF 4 SCI 1 EMA	1 NF (90 mm) 4 MCI 2 EMA 1 MNF

[a] No usable results were obtained by this instrument during this test.

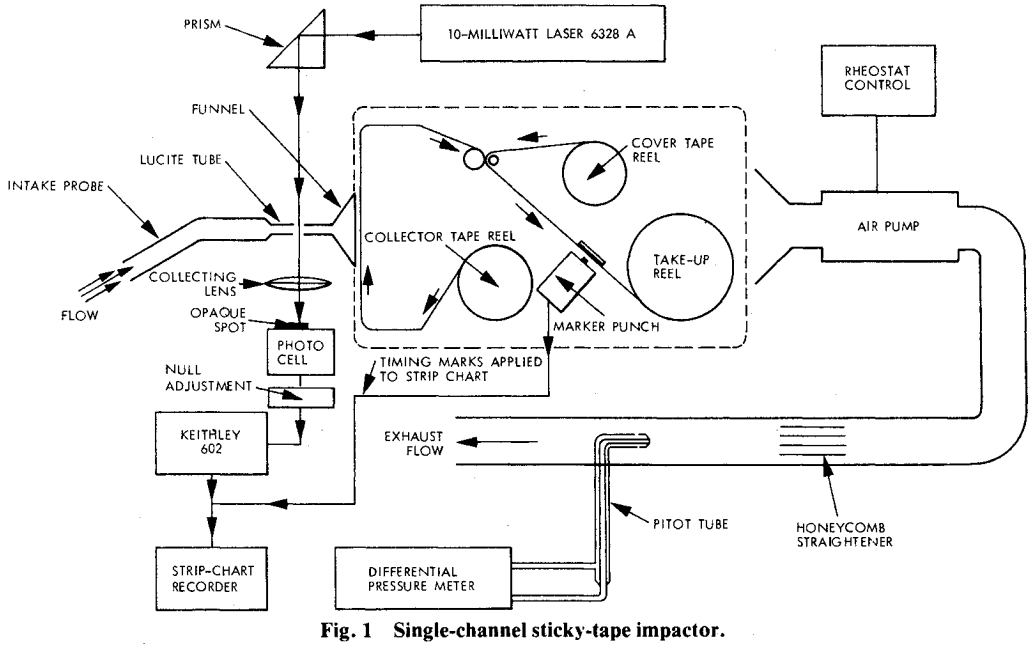

Fig. 1 Single-channel sticky-tape impactor.

creased range in particle sizes collected as compared with earlier attempts. The EMA has allowed considerable recent improvement in the accuracy with which submicron particulate populations can be counted and sized. The relatively large numbers of submicron particles collected during the investigation reported herein were not anticipated on the basis of earlier studies (cf. Ref. 2 in particular). However, in these earlier studies, primary interest was often centered on rocket motor performance and, hence, only on particles whose diameters were at least several microns.

Ground Cloud

The monitoring aircraft employed in the ground cloud was an Air Force Flight Test Center UH1N helicopter from Edwards Air Force Base, Calif. The monitoring instrumentation changed as the test program progressed.

The quartz-crystal microbalance particulate mass monitor was located in the inlet pipe of the grab samplers and was used principally as an indicator for timely operation of the grab sample valve.

The inability of the quartz-crystal mass monitor to discriminate between solid and liquid particulate deposition from the ground cloud, and its sensitivity to evaporation of the liquid collected, led to abandonment of this mode of measurement.

The single-channel sticky-tape impactor is shown schematically in Fig. 1 and is described in Ref. 4.

A Thermo-Systems, Incorporated, Model 3030 Electrical Aerosol Size Analyzer,[5] also called an electrical mobility analyzer, and its auxiliary equipment were installed in the helicopter for the last two missions at the WTR.

Using the diffusion charging-mobility analysis principle,[6-9] this instrument, under ideal conditions,[7] is capable of rapid, in-flight, size-distribution measurement of aerosols that contain particles between 0.003- and 1-μm diameter.

An entire measurement sequence takes approximately 2 min. Because the time for the helicopter to make a single pass through the rocket exhaust cloud is much less than the time for the instrument to make a complete size-distribution scan,

a grab-bag sampling technique was devised. At the desired time, ram air fills the 5-gal plastic bag. The captured aerosol sample is then admitted to the EMA for size analysis, evacuating the bag in the process and, thus, preparing it for the next pass through the cloud.

The previously used grab samples were replaced with one 90-mm-diam Nuclepore filter in a Millipore filter holder, mounted in parallel with the inlet system to the EMA grab bag. On command, the vacuum pump for the EMA could draw an aerosol sample across the 0.1-μm-pore Nuclepore filter.

HCl monitoring experiments were carried out by the Vandenburg AFB Space and Missile Test Center, and have been described in Refs. 10 and 11.

Stratospheric Plume

A U-2 aircraft was used to monitor the stratospheric plume during 1974 and 1975. It was instrumented with the following monitoring equipment for the April 10, 1974 Titan IIIC firing at the WTR: an audio tape recorder for recording the pilot's comments; a 90-mm-diam, 0.8-μm-pore-size Nuclepore filter sampler for obtaining an integrated particulate sample; a multiple-channel sticky-tape impactor; and a panoramic camera for photographing the missile contrail from launcher to high altitude.

For the October 29, 1974 and later monitoring flights, the single 90-mm-diam filter was replaced by the multiple-filter system shown pictorially and schematically in Fig. 2. It consists of six 25-mm 1-μm-pore-size Nuclepore filters, separated by bypass slots, mounted on a motor-driven rotor within a filter housing. The new system allowed an unexposed filter to be rotated into position and a sample collected for individual passes through the exhaust plume. Two vane-type vacuum pumps maintained isokinetic flow through a 1.07-mm-diam inlet orifice.

The EG&G, Inc. multiple-channel sticky-tape impactor was mounted in a pod under one wing of the U-2. Essentially, it consists of five single-stage tape impactors mounted in parallel and fed by ram air rather than a pump. The MCI and its enclosing pod are shown schematically in Fig. 3. The five tapes allowed a greater volume of the sparse stratospheric aerosol to be sampled.

Prior to the October 29, 1974 Titan IIIC launch from the WTR, an electrical mobility analyzer was installed in the U-2 airplane. This instrument was modified by the manufacturer according to specifications furnished by the developers of the measurement technique at the University of Minnesota to allow operation at an ambient pressure of 3.4 N/cm^2 (4.8 psia), which was the aircraft instrument bay pressure at 20 km.

The EMA was incorporated in a test system designed to collect automatically an aerosol sample and analyze it for size following test initiation by the pilot of the aircraft. The test system is shown schematically in Fig. 4 and is described in Ref. 4.

As indicated in Table 2, valid data were obtained from the U-2 mounted EMA on May 20, 1975 at the ETR and on June 8, 1975 at the WTR immediately following successful Titan IIIC launches on those dates. The only useful data obtained from the helicopter-mounted EMA were recorded in conjunction with the latter launch.

Equipment Calibration

The particulate monitoring equipment can be divided into three major categories: 1) instruments for qualitatively indicating the concentration of the incoming aerosol (quartz-crystal mass monitor and photoelectric cloud detector), 2) devices for simply collecting a quantity of material for later analysis (grab samplers), and 3) instruments for either measuring the size distribution in flight (EMAs) or collecting the material for later size analysis (sticky-tape impactors and 90-mm and multiple-filter samplers) in the laboratory. Only the instruments in the third category received quantitative calibrations.

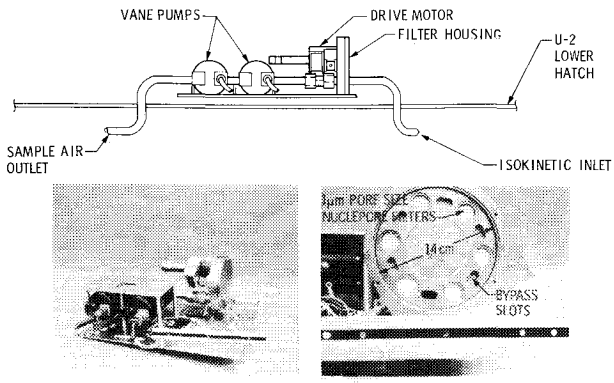

Fig. 2 Multiple-filter sampler.

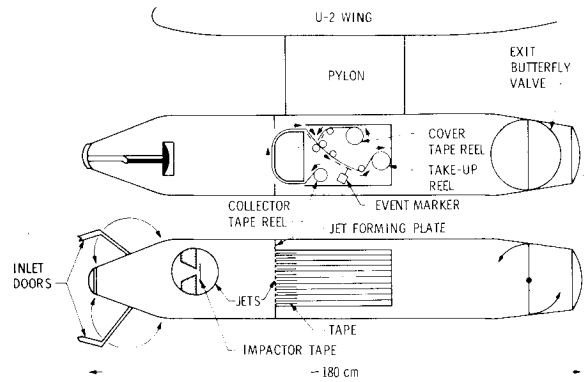

Fig. 3 Multiple-channel sticky-tape impactor.

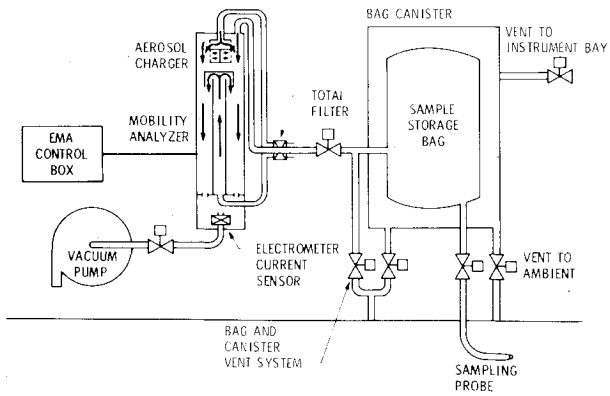

Fig. 4 High altitude electrical mobility analyzer system.

Filter Samplers

The calibration factor required for each impactor instrument (the Nuclepore filter samplers are essentially impactors) is the particle collection efficiency as a function of diameter. For the filters, the assumption is made that the collection efficiency is 100% for particles larger than the filter pore size, and drops off exponentially with decreasing particle diameter below the pore size. In reality, it has been shown[12] that a high collection efficiency can persist for particulate diameters significantly below the pore diameter, the actual values depending on the aerosol face velocity. A calibration in accord with the method of Ref. 12 was established analytically; however, because of the relatively few data collected by means of the filters, application of the calibration was never warranted.

Sticky-Tape Impactors

Because the program was curtailed in mid-FY'76, time and funding were insufficient to allow the collection efficiency of the SCI to be experimentally determined. However, it was found that, as an economically feasible alternative, published data regarding the collection characteristics of closely similar impactors (in particular, see Refs. 13-19) could be utilized to

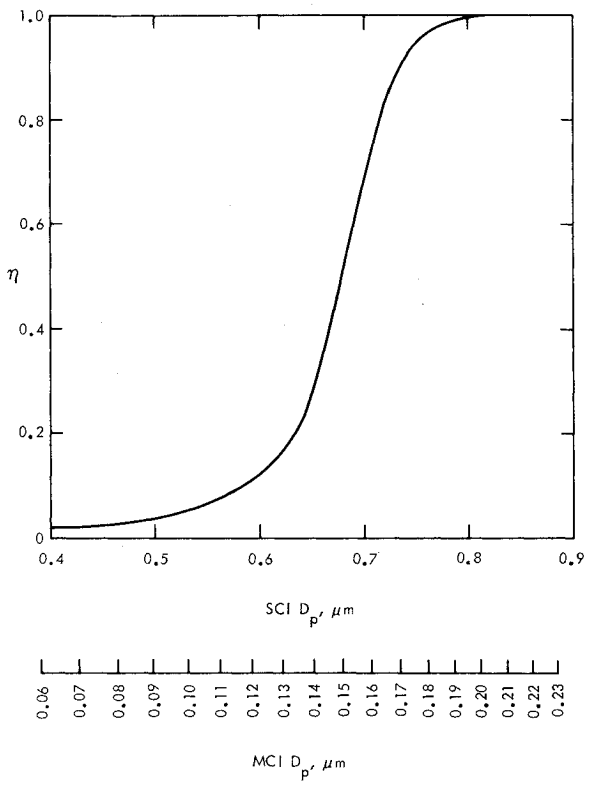

Fig. 5 SCI and MCI collection characteristics.

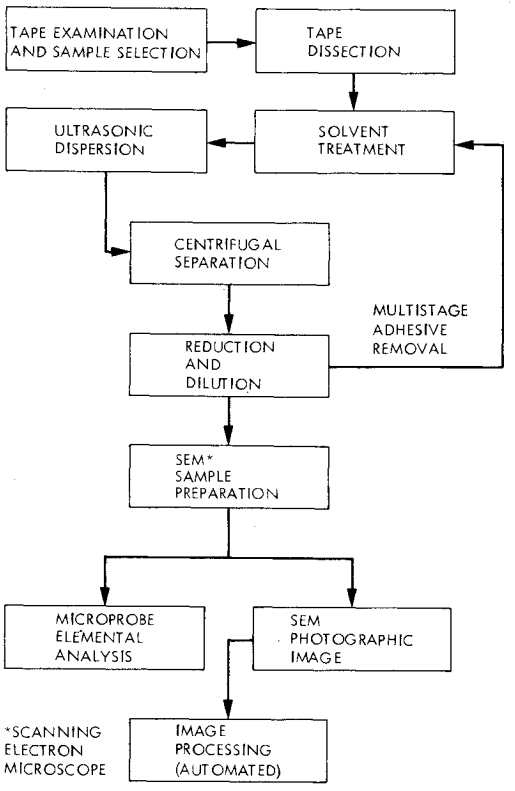

Fig. 6 Sticky-tape data processing procedure.

provide a sufficiently accurate assessment of the collection efficiency for the sticky-tape impactors used in this program. Impactor stage collection efficiency is plotted as a function of particle diameter in microns in Fig. 5 for the nominal operating conditions of the SCI, i.e., at near-sea-level altitude and 60 knots true air speed. In making this calculation, it was assumed that all particles were solid spheres of Al_2O_3.

The MCI-collected data presented in the Experimental Results section were collected at an altitude of approximately 20 km, and at a true air speed of about 200 m/s; a second scale of abscissa corresponding to the operating characteristic of an MCI stage is shown in Fig. 5. The reader is cautioned that this second scale is not quite linear.

Electrical Mobility Analyzers

The EMAs were calibrated against a "standard" instrument at the factory and, in the case of the EMA installed in the U-2, corrected for operation at the relatively low pressure that exists in the instrument bay when the aircraft is operating at a 20-km altitude. The calibration technique used for this "standard" instrument (the prototype of the present instrument) is described in detail in Ref. 8. Since the method of size analysis employed by this instrument is, in principle, independent of the other particulate physical characteristics (density, refractive index, etc.), the factory calibration was presumed to be adequate.

Because of the particle size range analyzed by the EMAs, it was necessary to consider the loss of sampled material in the aerosol induction system. Only the sampling tube system associated with the EMA carried in the U-2 was rigorously analyzed using the methods of Refs. 19 and 20. The corresponding system in the UH1N was estimated to result in relatively less severe modifications of the aerosol sample composition and size distribution than was calculated for the U-2 system. It is probably worth mentioning at this point that a cursory analysis of this same sort was required for the UH1N-borne SCI sample induction tube system; again in this last-mentioned case, the effect of the induction system was estimated to be not serious over the particle size range of interest.

Sample Processing Procedures

To place the results obtained during this investigation in proper perspective, not only must the data collecting apparatus be described and analyzed, as has been attempted in preceding sections, but the methods employed to obtain reduced results from raw data must be described.

Sticky-Tape Impactors

Following exposure of the sticky tapes and their immediate subsequent sealing by the cover tape and rewinding under flight test conditions, extensive processing was required to derive a corresponding particle size distribution. Figure 6 presents the tape-processing procedure in flow-chart format. All operations were performed under clean-room conditions.

Extracting the collected particulates from the sticky-tape adhesive proved to be very difficult. Several processes were tried before a suitable combination of solvents, separation equipment, and methods was found.

Two rather distinct analyses of the resulting sample were performed in the electron microscope. In the scanning mode, an SEM image or series of images, often at two or more magnifications (e.g., 200× and 20,000×) and at several sites on the stub surface, was obtained. In the microprobe mode, an elemental analysis of individual particles was accomplished by the spectral resolution of x-radiation emitted by the particle under excitation by the electron beam.

Because of the very large numbers of particles that had to be classified by size interval and counted in each SEM image, the need for an automated method for counting and sizing particles was soon recognized, and implementation of a computer-aided method for accomplishing this task was initiated. In this automated method, an oblique SEM image (such as Fig. 7) is processed to enhance the limb of each side-lighted particle (as shown in Fig. 8). The curvature of each limb and the corresponding diameter of the associated particle is then determined by an automated photoscanning process; the end result is a record of particle population and size distribution as determined for the particular image processed. Although this automated system for particle counting was

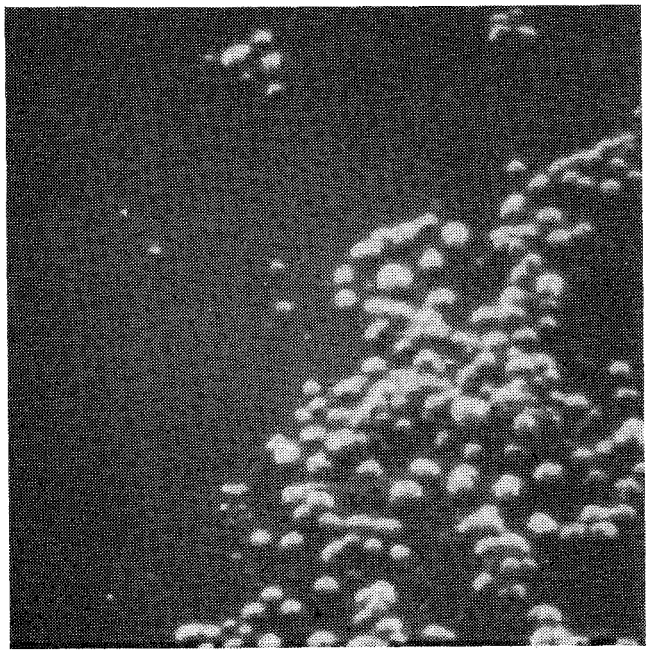

Fig. 7 Typical image from scanning electron microscope.

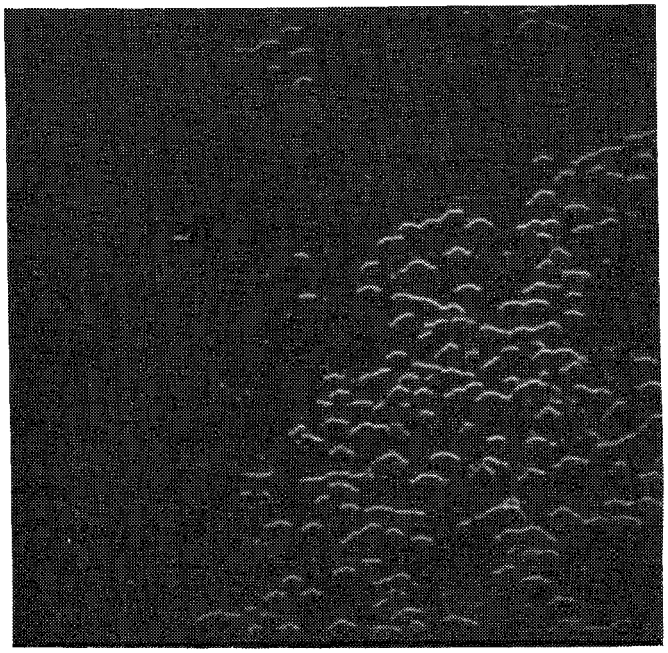

Fig. 8 Computerized edge determination of Fig. 7 image.

used successfully in several trial cases,[21] some limitations in the process (edge-identification criteria) remained when the particulate investigation reported in this discourse was terminated, and, as a result, only a limited number of automated particle counts were made.

Electrical Mobility Analyzers

The recorded analyzer data were converted to particle concentrations using the University of Minnesota chart method.[22]

Experimental Limitations

It is appropriate at this point to attempt to iterate certain practical limitations that affected the experimental methods of data collection and processing, but were recognized only as the data were being reduced.

Sticky-Tape Impactors

In calculating the impactor collection efficiencies (Fig. 5) that were used to correct the experimental results, it was assumed that all particles were solid spheres of Al_2O_3. In reality, it is known that the particles generated by an SRM are, in some cases, agglomerated, and/or the spherules are hollow.[23] Furthermore, it is known tht rapid cooling of the ground cloud results in condensation of some of the vapors generated by the SRM, and that the Al_2O_3 particles can serve as centers for the heterogeneous nucleation of these vapors.[24] If the Al_2O_3 particles act as nuclei for condensable vapors in the ground cloud, the dynamics for the collection of particles by the SCI will not be the same as they would have been for the same particles devoid of condensate. Also, the ultrasonic dispersion in the sample processing procedure will tend to break up collected agglomerates of ultrafine particles and result in their being counted as individual particles. Each of these effects must result in corresponding errors in the SCI determination of the Al_2O_3 particle-size distribution.

As indicated earlier, the adhesive from the sticky tape used in making these collections was not easily dissolved and washed from the collected solid residues. Furthermore, it was soon discovered that the adhesive of the unexposed sticky tape purchased from commercial suppliers was, in itself, an abundant source of extraneous, submicron particles. Fortunately, the number of these particles embedded in the sticky-tape adhesive that were large enough to have allowed their capture by the impactors under flight-test conditions appears to have been much smaller than the numbers of similar-sized particles that actually were captured by impaction on the tape in flight tests.

Electrical Mobility Analyzers

Four salient advantages of the EMA over the sticky-tape impactor are 1) the EMA determination of particle size is made as the particle passes through the analyzer chamber; 2) the particle-size determination depends only on particle diameter in the case of spherical particles, i.e., particle apparent density does not affect size determination; 3) the EMA is capable of measuring particles of smaller size than the minimum that can be reliably measured by the sticky-tape impactor; and 4) no particle-collecting substrate that might contribute additional particles and thus distort the determination of particle population or size distribution is required by the EMA.

On the other hand, as used in this investigation, it was necessary to rely on the manufacturer of the EMA to furnish a proper calibration for the instrument. Furthermore, the *outside* diameters of any aluminum oxide particles onto which hydrochloric acid has condensed are determined by the EMA; this may affect the particle-size distribution, and thus contribute to a disagreement between determinations made by the EMA on the one hand, and the sticky-tape impactor on the other. This effect is probably insignificant in the case of measurements made in the stratospheric plume, but may be appreciable in the case of measurements made in the ground cloud. A third limitation affecting EMA results was imposed by the method of sampling employed. Three to eight seconds were required to fill the EMA sample bag, and, at the nominal flight speeds and estimated initial exhaust plume diameters extant at either low or high altitude, only 5 to 10 s were required to traverse the contrail; therefore, the particle concentration as measured for the entire contents of the sample bag by the EMA probably sometimes included gases drawn from the mixing zone between contrail and ambient air and/or from the ambient air alone.

The sticky-tape impactor results are also limited in this last-mentioned way; in the case of the SCI, the tape exposure time was 30 s while, in the case of the MCI, the tape exposure time was about 11 s.

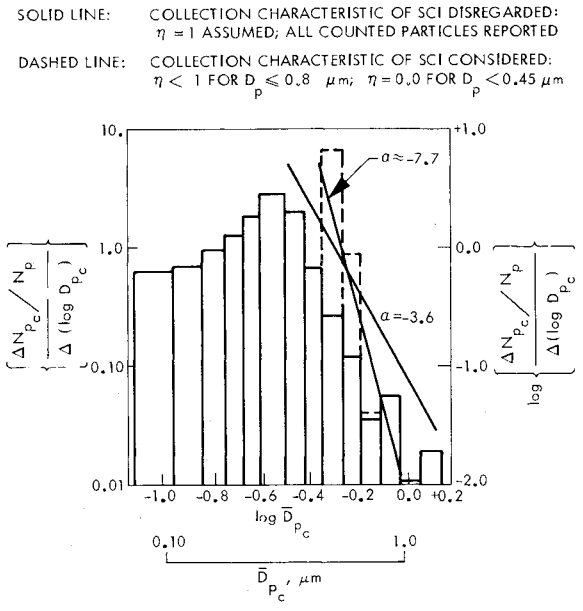

Fig. 9 Helicopter SCI results for July 13, 1973 launch, $T+23.0$ min.

Experimental Results

Size Results from Particulate Sampling of the Ground Cloud

Figure 9 shows results obtained from the UH1N-borne SCI on July 13, 1973 at 23 min after launch of a Titan IIIC from the WTR.

The initial data reduction was made without an accurate evaluation of the impactor cutoff characteristics; thus, particles as small as 0.0562 μm in diameter were counted, even though the SCI capture efficiency is only about 0.039 for particles 0.504 μm in diameter. The large fraction of particles smaller than 0.472 μm that were counted must thus be attributed to the dispersal by the tape dissolution process of particles collected as aggregates and/or to material already present on the sticky and cover tapes when they were used to capture the Titan IIIC ground-cloud particulates. The histogram indicated by the solid lines in Fig. 9 corresponds to the preliminary analysis.

When the data discussed above were corrected for impactor efficiency and only particles larger than 0.472 μm after elution from the tape were considered in the analysis, the results, where they differed from the earlier analysis, are those indicated by the dashed lines and, again, by the solid lines where no difference was perceptible.

The exponent α obtained by fitting the commonly used particle size distribution model of Junge (cf. Eq. 3.21 of Ref. 20)

$$\frac{d(N_{pc}/N_p)}{d(\log r)} = Cr^{-\alpha}$$

to the large particle sizes of the earlier results, is

$$\alpha \approx -3.6$$

while, for the later results,

$$\alpha \approx -7.7$$

The value of α as determined from the uncorrected data is much nearer to typical values predicted and measured over about the same particle size range in other patently similar studies,[1,25,26] and to the value determined by EMA in this case (reported below), than is the value of α determined from the partially corrected SCI data.

If the value of α determined from the so-called corrected results is in serious error (as seems likely), the principal source of this error is probably the very small number of particles (i.e., 144) counted in the size range that was measurable by the SCI.

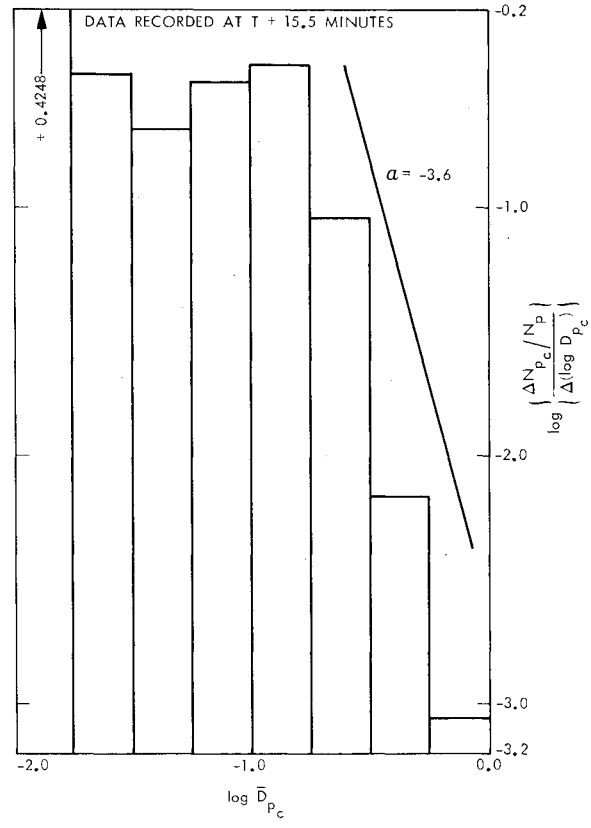

Fig. 10 Helicopter EMA results for June 8, 1975 launch, $T+15.5$ min.

Figure 10 presents results obtained from the UH1N-borne EMA on June 8, 1975 at about 15.5 min after the launch of a Titan IIIC from the WTR. As indicated on Fig. 10 for $D_p \geq 0.1$ μm, $\alpha \approx -3.6$ appears to fit the data reasonably well.

To show all the data collected by EMA in this field test, Fig. 11 was constructed. This figure includes histograms corresponding to data collected by helicopter 27 min and 45 min after launch. It is clear from this figure that, for 0.01 μm $\lesssim D_p \lesssim 0.1$ μm, the rate at which the number of particles in a given bandwidth of particle diameters decreases with particle diameter is much lower than is evident for $D_p \geq 0.1$ μm. While it cannot be stated unequivocally, the available data indicate that the number of particles in a given bandwidth of particle diameters is, to the accuracy of the results, virtually constant for 0.01 μm $\lesssim D_p \lesssim 0.1$ μm. Figure 11 also seems to indicate no significant trend in particle size distribution with time after launch in the Titan IIIC exhaust ground cloud. The standard deviations of the ordinate corresponding to the particle size band of the $T+15.5$ histogram are included in Fig. 11. From these, it is inferred that variations in the histograms corresponding to different times may be due to spatial rather than temporal variations in the particle size distributions within the ground cloud.

Size Results from Particulate Sampling of the Contrail at Approximately 20-km Altitude

The results obtained from the U-2 borne particulate measuring instruments are of considerably higher quality than those obtained from similar UH1N-borne instruments. Several valid reasons for this difference can be cited:

1) Because the program was terminated rather abruptly, many SCI data acquired in later field tests were not evaluated; thus, only the SCI data obtained in the first field test with this instrument were reduced and incorporated into this report.

2) The sample induction systems employed with the UH1N-borne SCI and EMA systems were not so simple as the corresponding induction systems carried by the U-2; thus, the

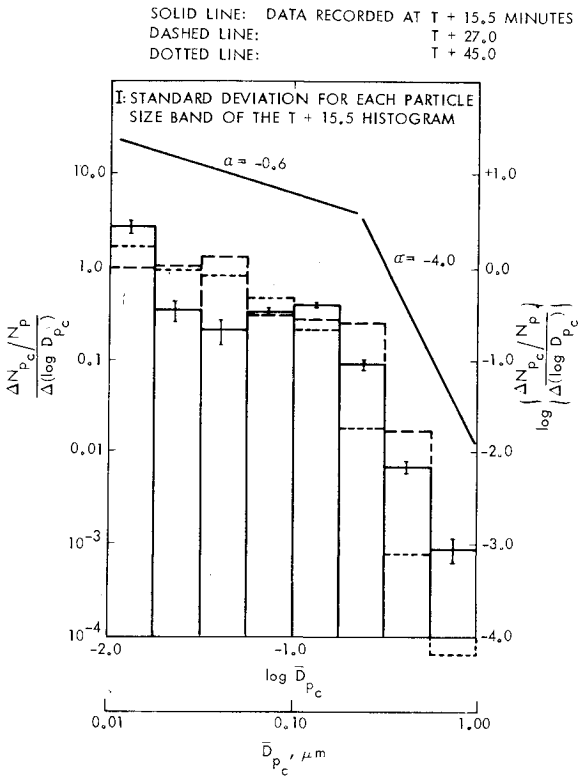

Fig. 11 Helicopter EMA results for June 8, 1975 launch.

losses of particulates in the induction systems carried by the UH1N have not been as precisely estimated as they have been in the case of the U-2.

3) The formation of the Titan IIIC ground cloud in the presence of an ambient sea-level atmosphere composed of marine air undoubtedly leads to further nucleation of water droplets, at least in the vicinity of the ground-cloud boundaries. Furthermore, on some flights, naturally occurring haze and low-lying clouds made identification of the ground-cloud boundaries uncertain at best. In contrast to these problems at low altitude, observation of the Titan IIIC contrail in the stratosphere was not obscured by clouds, and the absolute humidity of the ambient stratospheric atmosphere was much, much lower than that of the expanded contrail; thus, it was possible to extract samples from the central region of the contrail with reasonable confidence that boundary effects exerted a relatively small influence on the results.

Figure 12 presents results obtained with a U-2 borne oiled-wire impactor fielded by the NASA Ames Research Center (ARC) at the WTR on April 10, 1974. A second U-2 carried the MCI as part of the JPL-fielded test effort conducted in conjunction with this same flight, and results obtained with this impactor are presented in Fig. 13. Since the data were collected almost concurrently—the ARC data were collected at about 13 min after launch, and the JPL data, 15 min after launch—and at only slightly different altitudes, comparison of the results is warranted.

It is encouraging to note the virtually identical values determined for α by the two contemporaneous measurements of particle size distribution, cf., Figs. 12 and 13. Even more exciting is the similarly bimodal character of the independent measurements: α approximately equal to -4 for submicron particles and -2 for particles >0.3 μm. This bimodality is shown even more dramatically when the distributions are plotted on a volume or mass basis.

The study of aluminum oxide product collected from solid-propellant burners also has shown a complex, multimodal size distribution structure.[27,28] The results are attributed to the multiple mechanisms forming the aluminum oxide: accumulation of oxide present on the unburned aluminum, condensed-phase oxidation, vapor-phase oxidation, and

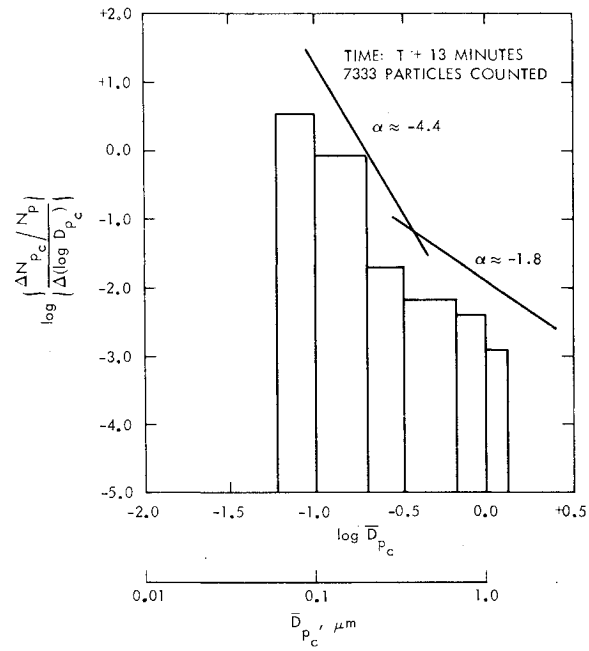

Fig. 12 NASA Ames Research Center oiled-wire impactor results for April 10, 1974 launch.

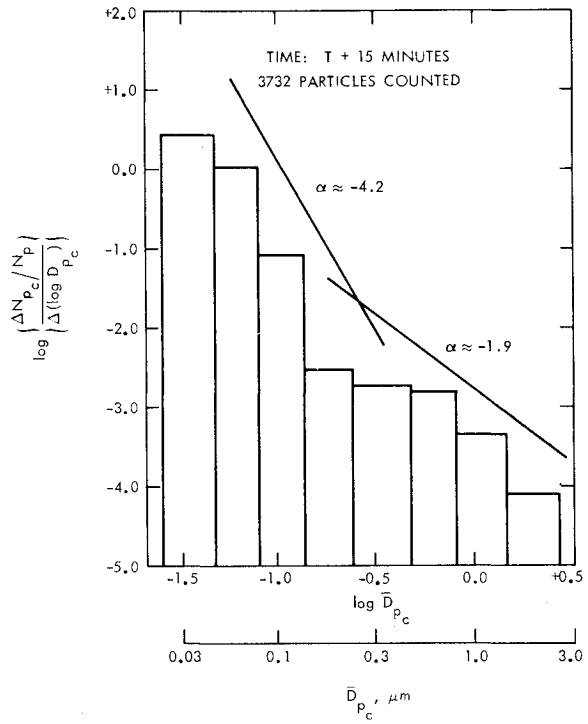

Fig. 13 U-2 MCI results for April 10, 1974 launch, $T+15$ min.

shedding of particles (hollow spheres in particular). A majority of the oxide droplets are the submicron "smoke" produced in the vapor-phase flame.[29]

The EMA results presented in Figs. 14 and 15 are consistent with the slope exponent data of Figs. 12 and 13. Defining a comparable upper mode for the larger particles is difficult, however, because of the 1-μm upper size limit of the measurement instrument. It is interesting to see, in Fig. 15, that a noticeable increase in the fraction of particles for which $0.3\ \mu\text{m} \lesssim D_p \lesssim 1.33$ has occurred between $T+7$ and $T+13$ min in both the test of May 20, 1975 and that of June 8, 1975. Since it is improbable that the solid particles grew under the conditions then prevalent in the contrail, such growth, if it did in fact occur, must reflect the growth of particles due to condensation of vapors on the already generated nuclei, or to

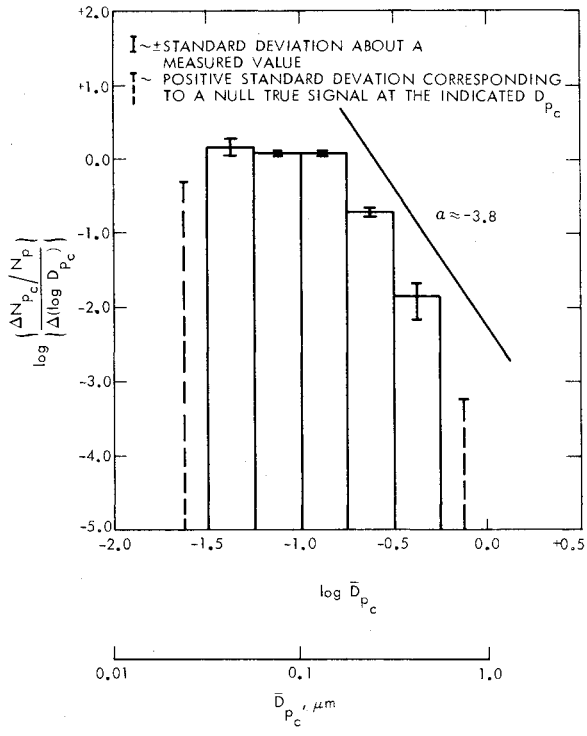

Fig. 14 U-2 EMA results for May 20, 1975 launch, $T+7$ min.

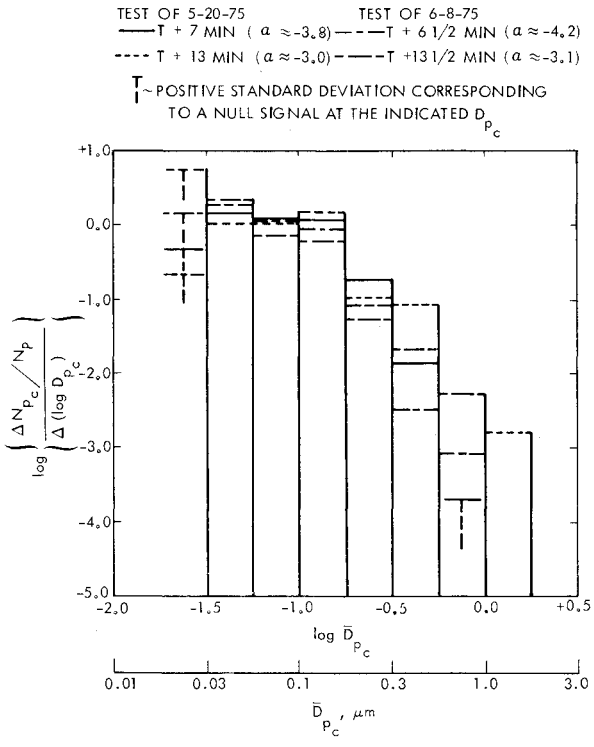

Fig. 15 U-2 EMA data collected at approximately 20 km.

particle agglomeration. Even these further explanations for the noted increase in particles of the size range indicated above would be unconvincing were it not for the fact that the vapor mixture in the contrail contained hydrogen chloride and small amounts of iron and aluminum compounds as well as water vapor; the particles may have been more strongly deliquescent than would pure H_2O and Al_2O_3 nuclei.

Total Concentration

The EMA can give absolute concentration when the sampling time is shorter than the transient time through the plume, but, as mentioned in the previous section, it is not clear whether or not such conditions existed. The measured particle concentration at 19 km dropped from approximately 10^9 particles/m^3 at $T+7$ min to 10^8 particles/m^3 at $T+13$ min for the May 20, 1975 monitoring flight. For the June 8, 1975 launch, the concentration values were approximately 10^{10} and 10^9 particles/m^3, respectively. These latter values are of the order of theoretically predicted values, and, therefore, a reasonable, predicted concentration for calculation purposes is about 10^{10} particles/m^3 in the early plume.

Density

Very preliminary measurements were performed with a gravimetric technique to determine the density of the particles collected. Several authors reported that many of the Al_2O_3 spheres collected from rocket firings have hollow interiors and therefore, an apparent or aerodynamical density inferior to the theoretical density of about 3.97 g/cm^3. The preliminary measurements have yielded a wide range of densities from 1.5 to 3.5 g/cm^3.

Appearance

Most of the particles examined were spherical. Occasionally, a sphere with a coating of agglomerated smaller spheres was found—for example, a 10-μm sphere with perhaps 50 0.1-μm particles on its surface. Various textures have been observed, from smooth at a resolution of 20 nm to finely grained and deeply grooved, indicating a polycrystalline structure.

Structure and Composition

The cyrstalline structure of the Al_2O_3 particles was examined by EMS Laboratories, Pasadena. The structure was found to be hexagonal (α phase) for particle diameters of a few tenths of microns. Both transmission and reflection electron diffraction methods were used. Significant amounts of Fe_3O_4, presumably from a propellant additive used to control the burn rate, were also found. However, earlier transmission diffraction measurements on just a few 0.1-μm particles collected with an impactor showed a cubic (γ) structure for the Al_2O_3. Other measurements on material collected from small motors fired in a closed tank also indicated a cubic structure. At present, it would appear that the evidence indicated a hexagonal (α) structure for the Al_2O_3 particulates injected into the stratosphere.

Elemental composition of the particulates was obtained by x-ray fluorescence; besides aluminum and occasionally potassium, sodium, and titanium, significant quantities of iron and silicon were found. Very rarely has Cl been observed by x-ray fluorescence. However, a series of samples collected on Nuclepore filters and analyzed by electron spectroscopy (ESCA) revealed a significant, often large, signal from Cl in degrees of oxidation varying from a tight bond (as in a chloride) to a free atom (as for surface adsorption). It was reported in the literature that such a variability in the bond energy of Cl deposited on metal surfaces is normal and dependent on the Cl surface concentration. From the ESCA shift of the aluminum peak, it is presumed that $Al_xCl_yO_z$ compounds may have been formed.

The apparently contradictory evidence for Cl obtained by electron spectroscopy and x-ray fluorescence can probably be best explained by the different penetration capabilities of the two techniques. The typical signal for x-ray fluorescence originates from a layer ranging from 0.5 to 5 μm in thickness, whereas the ESCA signal is produced in only a few nanometers. If it is hypothesized that Cl is not uniformly distributed in the molten Al_2O_3, but is deposited on the surface after the particle has frozen, forming an almost complete monolayer, one has a situation in which ESCA may detect 10% to 20% Cl in the first few layers, but in which the relative x-ray yield of this small surface layer of Cl, averaged

over a layer 0.5 to 5 μm thick, would be undetectable. It is unknown whether, under some conditions, the less tightly bound portions of such a layer can be released to the surrounding stratosphere.

Summary and Conclusions

It is concluded that for both the ground cloud and the stratospheric plume, the bulk of the particles are in the submicrometer range, typically 10^{-5} cm in diameter, whether a number, surface, or volume average is utilized. This new finding contrasts with widely quoted, previous estimates that the mean diameter is of the order of 10^{-3} cm. The immediate and obvious consequence is that the typical residence times in the atmosphere are much longer (about two orders of magnitude) than earlier estimates have indicated.

Number concentrations in the early plume of the order of 10^{10} particles per cubic meter are probably correct. Other properties of the particulate components in the exhaust contrail are less certain, and the results should be viewed as preliminary.

Acknowledgments

This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract NAS7-100, sponsored by the National Aeronautics and Space Administration.

The following assistance is gratefully acknowledged: Edwards Air Force Base for supplying monitoring aircraft and test support; Vandenberg Air Force Base for their cooperation and technical support; NASA Kennedy Space Center for test support; EG&G, Inc. for supplying the sticky-tape impactors and test support; University of Minnesota Particle Technology Laboratory for developing high-altitude modifications for the Electrical Mobility Analyzer; Thermal Systems, Inc. for performing high-altitude EMA modifications, and for assistance throughout the program; Meteorology Research, Inc. for supplying high-altitude EMA test system and test support; University of Southern California Image Processing Institute for development of automated particle-counting technique; JPL Test and Mechanical Support Section for high-altitude test facilities and support; and JPL Propulsion Systems Section for clean-room facilities and support.

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