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Hydrogen Chloride Measurements in the Space Shuttle Exhaust Cloud—First Launch, April 12, 1981

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Partitioning of hydrogen chloride between the aerosol and gaseous phases in the first Space Shuttle exhaust cloud was experimentally investigated as the exhaust cloud was diluted with ambient air. Airborne measurements were obtained of gaseous hydrogen chloride (HCl), total HCl, relative humidity, and temperature to determine the conditions controlling HCl aerosol formation in the Shuttle exhaust cloud. Two segments of the cloud, each at a significantly different relative humidity, were monitored. Equilibrium predictions of HCl aerosol formation agreed with the measured HCl partitioning at the higher and lower relative humidity conditions, but do not agree at the aerosol formation threshold region. Measurements were taken in the Shuttle exhaust cloud from 8.6 min until 2 h and 8 min after launch. HCl concentrations ranged from 17.5 to 0.9 ppm and relative humidity from 86% to less than 10%.

Introduction

SIGNIFICANT quantities of hydrogen chloride (HCl) along with other exhaust products are released in the Earth's atmosphere during each Space Shuttle launch. The amounts of the principal exhaust constituents remaining in the ground cloud at stabilization are estimated in Table 1. Hot exhaust effluents, produced during the launch of the Space Shuttle, mix with the surrounding ambient air and rise because of buoyant forces. After rising for 4-15 min after launch, the cloud usually stabilizes at the top of the boundary layer, depending on the meteorological conditions.

The purpose of this study was to measure directly the partitioning of HCl between aerosol and gaseous phases in the exhaust cloud, as the cloud was diluted with ambient air. The experiment was carried out by making airborne measurements in the exhaust cloud produced during the Space Shuttle launch on April 12, 1981. In-cloud HCl concentration measurements using a gas filter correlator detector for the gaseous HCl and a chemiluminescence detector for the total HCl concentration in a mixture were made as the exhaust cloud drifted downwind of the launch pad. The difference between these measurements for a given sample is equated to the amount of HCl in aerosol phase.

HCl loss mechanisms in the cloud are directly related to HCl partitioning between the aerosol and gaseous phases. Some experimental results have indicated that if HCl is predominantly in the liquid phase, a considerable reduction in HCl washout occurs relative to gaseous HCl absorption by raindrops passing through the cloud. The larger the droplets, the less efficiently the HCl aerosol is scavenged by falling rain.[2] Aerosol formation is due to nucleation of the condensable vapor in the cloud. The nuclei may have any number of origins, including minute particles of aluminum oxide generated by the solid rocket propellant in the Shuttle boosters and foreign debris entrained in the cloud as it forms and diffuses. In a very moist cloud (100% relative humidity), the aerosol droplets could grow to such an extent that direct rainout of the HCl could occur. HCl rainout conditions were not observed during the measurement sequence of the experiment.

Experimental laboratory work relating to aerosol formation and partitioning of the HCl water vapor system is limited. Twomey[3] has measured the conditions under which HCl aerosol droplets grow in size, and Fenton and Ranade[4] have verified the conditions controlling the aerosol formation threshold in the laboratory. Gillespie and Johnstone[5] made measurements of particle-size distributions for HCl aerosols, and Knutson et al.[6] investigated the washout of HCl due to rain. Of particular interest to this study are the equilibrium calculations of Rhein[7] predicting HCl aerosol formation by the interaction of HCl with humid air. Rhein's analysis is based on tabulated data in the literature relating phase equilibrium to the partial pressure of HCl and H_2O, and for water-vapor pressure vs temperature.[8,9]

Analytical techniques used in this experiment were developed over a number of years, and were tested in exhaust clouds produced by Titan III launches.[10,11] The solid-propellant rocket motor of the Titan III produces approximately half the exhaust HCl of a Shuttle launch. Since similar proportions of HCl to other exhaust products are released in both Titan III and Space Shuttle exhaust clouds, these early Titan III experiments were also useful in verifying analytical models designed to predict the transport and physical-chemical state of in-cloud HCl.[12-15]

The National Aeronautics and Space Administration is actively engaged in studies to determine the effects of rocket motor firings on the environment in compliance with the National Environmental Policy Act of 1969. These studies are designed to obtain data for vehicles with solid-fuel rocket motors to be used in the establishment of potential launch constraints using model prediction techniques and to develop expertise in the areas relating to the environmental impact on launch activities.

Table 1 Space Shuttle exhaust constituents

Species	Amount, kg
Aluminum oxide	56,100
Carbon monoxide	240
Hydrogen chloride	35,200
Water	65,300
Nitrogen oxides	2,300
Carbon dioxides	76,800
Chlorine	4,000

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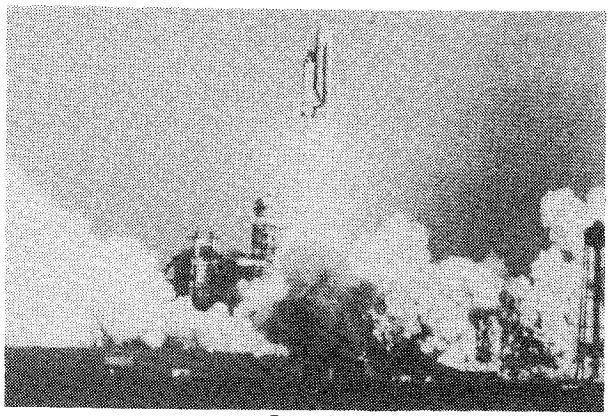
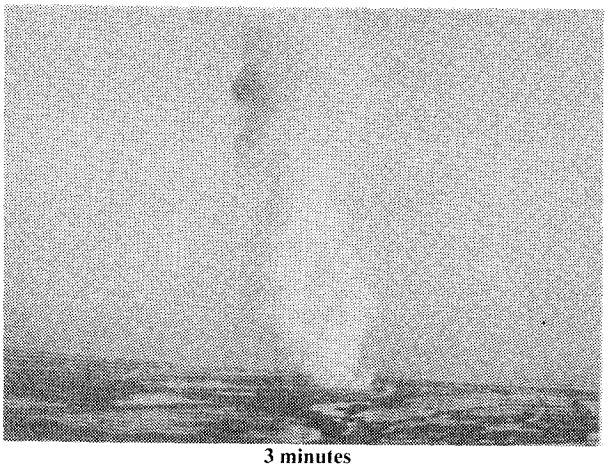
Experiment

Launching of the Space Shuttle produces a plume of hot exhaust effluents which mixes with the ambient air and rises because of buoyant forces, as shown in Fig. 1. These photographs, taken at launch and approximately 3 and 7 min after launch, illustrate the development of the exhaust cloud with time. Depending on the atmospheric inversion temperature gradient, the ground cloud will either stabilize as one cloud below the top of the mixing layer or segment into several clouds under weak inversion conditions. When segmentation occurs, each section of the cloud stabilizes at an altitude which is dependent on the time required for that part of the cloud to reach equilibrium with the ambient air temperature.

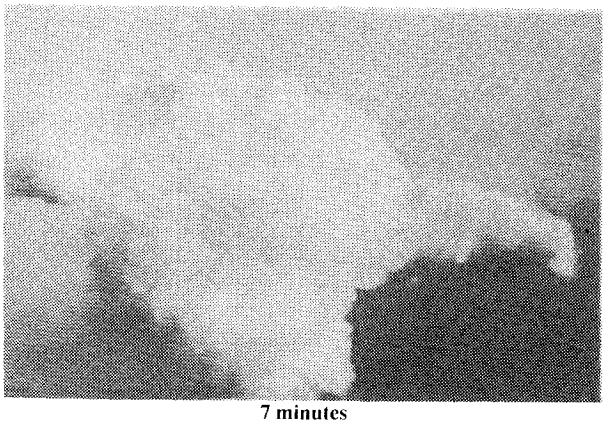
Segmentation of the Space Shuttle exhaust cloud occurred because of weak inversion conditions existing at launch time.



Launch



3 minutes



7 minutes

Fig. 1 Photographs of Space Shuttle exhaust cloud growth with time.

Relative humidity and temperature of the ambient air from rawinsonde measurements at 12 min after launch are presented in Fig. 2. The lack of a strong gradient in the temperature-altitude profile indicates a strong possibility that part of the exhaust cloud would pass through the boundary layer and break up at higher altitudes. The large variations in the relative humidity-altitude profile indicate that the cloud segments would stabilize at different levels of relative humidity as encountered during the airborne sampling.

After rising and mixing for about 8 min, the exhaust cloud, as expected, separated into at least five segments of various volumes and at various altitudes. Two parts of the separated cloud were selected for sampling in order to obtain the optimum range of relative humidities. The first cloud slowly drifted northward at altitudes from 650 m up to 950 m under high relative humidity conditions. The second cloud segment drifted westward at altitudes from 1350 m up to 1880 m under low relative humidity conditions.

Sampling passes were flown through the center of the lower altitude cloud every 2-5 min from 8.6 min until 45 min after launch. The higher altitude cloud was similarly sampled from 49 min until 2 h and 8 min after launch. Owing to easterly winds, the high exhaust cloud segment drifted from the Kennedy Space Center to Orlando, Fla., by the end of the sampling mission. Relatively clean and clear marine environmental conditions occurred over this area due to easterly winds which were continuous for several days before launch.

Instrumentation

A twin-engine light aircraft was equipped to monitor gaseous HCl, total HCl, relative humidity, and temperature.[16] In addition, routine flight parameters (altitude, heading, and air speed) were recorded. Total HCl measurements are based on a sequence of reactions which take place on the inner surface of a coated inlet tube to generate Br_2, which is then quantified by chemiluminescent oxidation of alkaline luminol. A comprehensive evaluation of the total HCl detector can be found in Refs. 11 and 17.

The gas filter correlator, used to measure gaseous HCl, is a nondispersive infrared absorption instrument which employs a concentrated sample of HCl to provide a selective filter for radiation absorbed in a gas mixture containing traces of HCl. Since this selective filter only absorbs radiation at particular wavelengths characteristic of gaseous HCl, this instrument will respond only to gaseous HCl and not to HCl in the liquid

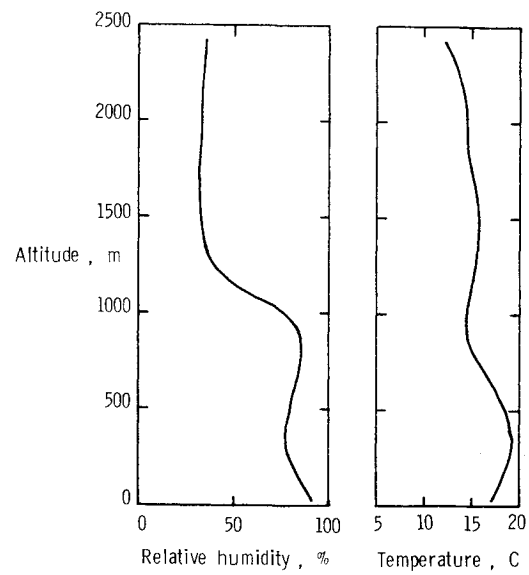


Fig. 2 Vertical profiles of temperature and relative humidity at Kennedy Space Center from rawinsonde measurements, April 12, 1981 ($T+12$ min).

phase. Details on the design and calibration of the gas filter correlator have been documented in Refs. 11 and 18.

Air samples for the HCl instruments are obtained through aircraft nose probes designed to provide freestream uncontaminated air samples. Isokinetic flow sampling inlets are provided for these probes, and they are aligned to be parallel to the freestream during sampling. Both HCl instruments are mounted in the nose compartment of the aircraft to minimize HCl losses in the inlet lines. In addition, the sampling inlet tube for the total HCl detector was designed to be used as the aircraft sampling probe. The gas filter correlator inlet line was Teflon, and the sampling cell was Teflon coated. Sample flow rates provide a sample volume exchange rate in the instrument's detection chamber of 6 per second and 3 per second for the total and gaseous instruments, respectively. Instrument lag times as a result of sample flow rates and short inlet lengths are both less than 1 s. The lower detection limit for both instruments for the April Shuttle measurements is approximately 0.2 ppm by volume.

Airborne Measurements

Within 8 min after launch, all parts of the segmented ground exhaust cloud stabilized at various altitudes depending on their internal characteristics and the local meteorological conditions. Two of the cloud segments were selected for sampling and gaseous and total HCl profiles along with temperature and relative humidity profiles were measured in each segment as it diffused with time. The lower altitude cloud segment was sampled until 45 min after launch and results from two sampling passes are shown in Figs. 3 and 4. The higher altitude cloud segment was sampled from 49 min until 2 h and 8 min after launch, and representative results are shown in Fig. 5. All data are plotted against time after launch.

During the first few aircraft passes, while rapid dilution of the cloud occurred, total HCl concentrations also decreased rapidly. Measurements obtained in the lower cloud segments (Figs. 3 and 4) show the total HCl to be considerably greater than the gaseous HCl, which indicates that a significant amount of HCl was present in the aerosol phase. The difference between total and gaseous HCl concentrations is seen in Figs. 3 and 4 to decrease with time. Relative humidity profiles measured during these two passes indicate a high relative humidity within the cloud segment which decreases with time and cloud dilution. Airborne relative humidity measurements outside the cloud occasionally differed from the rawinsonde measurements (Figs. 2 and 3). Variable low altitude meteorological conditions along the coast caused these differences. The airborne data are considered the most reliable and airborne relative humidity measurements within the cloud will be used in the analysis of the HCl measurements.

Measurements obtained in the higher altitude cloud segment (Fig. 5) show the total HCl and the gaseous HCl concentrations to be approximately equal, indicating no measurable aerosol HCl present. Relative humidity measured within the higher altitude cloud segment was significantly lower, as indicated by the rawinsonde measurements. Temperature was relatively constant during the measurement period.

HCl Aerosol Analysis

Partitioning of the exhaust cloud HCl into aerosol and gaseous HCl was compared with Rhein's predictions for HCl in humid air.[7] The curves in Rhein's paper were computed from data available in the literature in tabulated form, relating phase equilibrium to partial pressure of HCl and H_2O

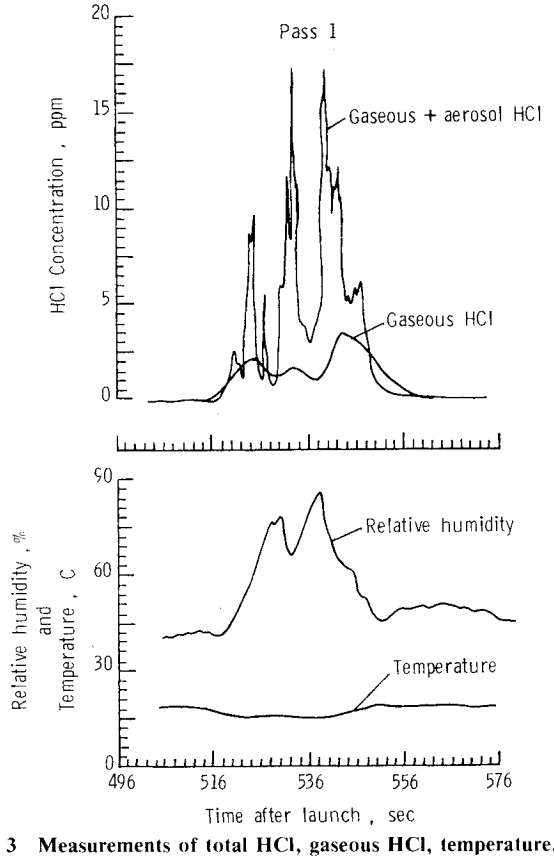


Fig. 3 Measurements of total HCl, gaseous HCl, temperature, and relative humidity from the first airborne pass through the lower altitude segments of Shuttle exhaust cloud.

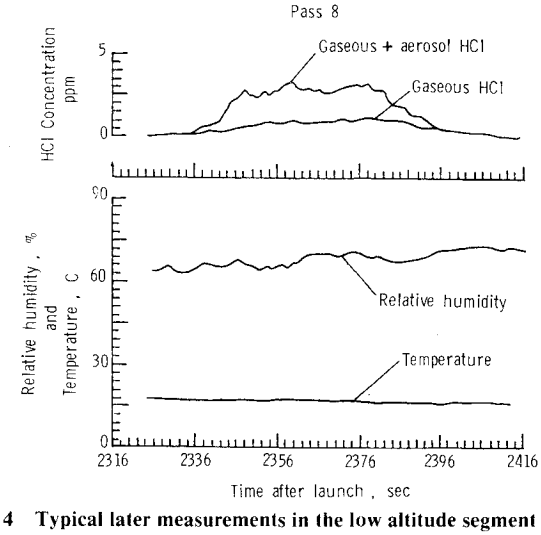


Fig. 4 Typical later measurements in the low altitude segment of the exhaust cloud at high atmospheric relative humidity.

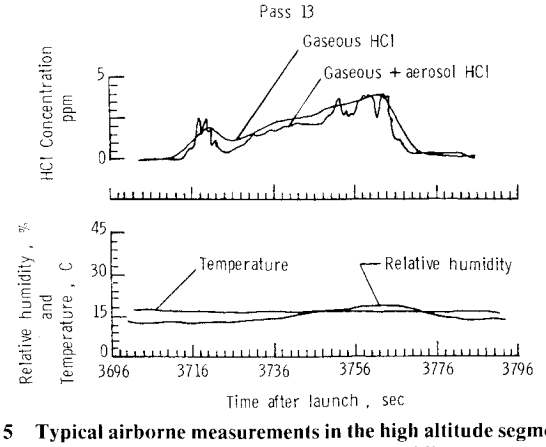


Fig. 5 Typical airborne measurements in the high altitude segment of the exhaust cloud at low atmospheric relative humidity.

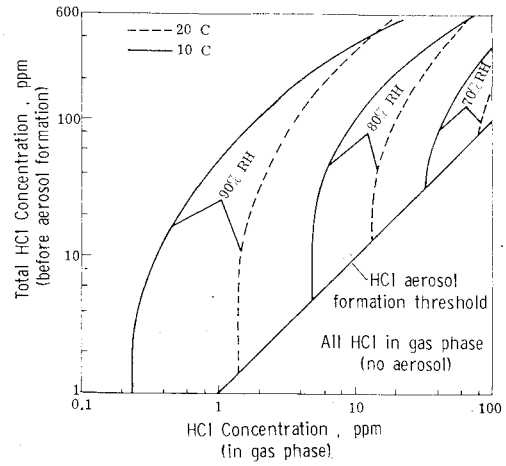


Fig. 6 HCl in gaseous phase vs total HCl as a function of temperature and relative humidity for hydrochloric acid aerosol formation in HCl and humid air.[7]

and for water vapor pressure vs temperature.[8,9] These aerosol formation predictions were replotted in Fig. 6 in order to clarify the analysis of the exhaust cloud measurements. Measured concentrations of total HCl were used in conjunction with Fig. 6 to obtain the predicted concentrations of gaseous HCl for a known temperature and relative humidity. The 45-deg line indicates the threshold for aerosol formation. The area to the right of this line is the region in which all HCl is in the gas phase. This plot indicates that aerosol formation is favored by lower ambient temperature and higher relative humidity, as may be expected. Although Fig. 6 indicates the conditions under which aerosol is anticipated, based on the system liquid-gas phase equilibrium, the actual formation of aerosols depends upon droplet nucleation. Nucleation sites are plentiful in a solid rocket exhaust cloud from both materials already present in the atmosphere and from Al_2O_3 exhaust particles.

Although the particulate matter present in the cloud is treated only as nucleation sites, these particles may play a role in increasing the range of stabilization of HCl in the liquid droplet phase at lower relative humidities and low HCl concentrations. Soluble nonvolatile particulate matter, such as sea salts, reduce the vapor pressure of water so that some of the cloud particles may still contain water at the lower relative humidities and thereby retain some HCl. Aluminum oxide dissolution has also been shown to be an effective HCl neutralization process in an acid aerosol droplet.[19] Since Al_2O_3 is present in significant amounts in the exhaust cloud, this process may also play a role in reducing the total HCl concentration. It is not possible to treat analytically the effects of soluble, nonvolatile matter on HCl stabilization at this time; therefore the results of this experiment were only used to evaluate the simplified equilibrium partitioning analysis as applied to exhaust clouds.

Partitioning between gaseous and aerosol HCl is not only affected by temperature and relative humidity, but is also a function of total HCl concentration as seen by the equilibrium analysis in Fig. 6 and the peak concentrations in Figs. 3 and 4.

A comparison between the data from both cloud segments and the equilibrium analysis is presented in Fig. 7, where peak HCl concentrations measured by both instruments during each airborne pass are plotted as a function of time after launch. Each data point on this plot represents the maximum value measured for a single pass at a specific time during the pass referenced to launch time. Relative humidity and temperature are also plotted. A solid line has been faired through the peak total HCl measurements for the low altitude, high relative humidity cloud segment. The decrease in total HCl concentration with time is a result of cloud dilution with the surrounding atmosphere. Chemical reaction of atmospheric

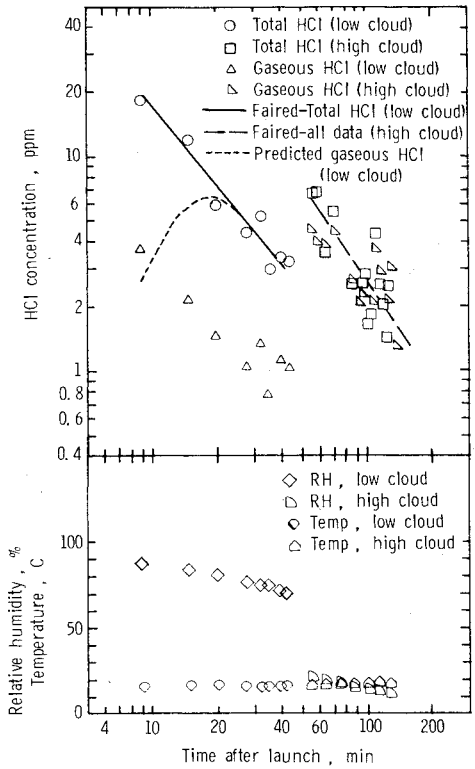


Fig. 7 Peak concentrations of gaseous and total HCl measured in two segments of the Shuttle exhaust cloud as a function of time. The lower figure indicates the peak temperatures and relative humidities also measured in the cloud segments.

HCl is relatively slow and is insignificant for the times of this experiment.[11] The measured values of peak total HCl concentration in the low altitude cloud were used along with the measured cloud values of temperature and relative humidity to predict the gaseous HCl distribution using the aerosol formation analysis of Fig. 6. This prediction of gaseous HCl distribution is shown as the short dashed line in Fig.7 and is seen to agree with the measured HCl concentrations only during the first pass which occurred at a very high relative humidity value in the cloud (87%). Measurements during the second pass show a gaseous HCl concentration lower than predicted.

After the second pass, the decreasing relative humidity and total HCl measurements lead to an equilibrium analysis prediction that all HCl should be in the gaseous phase since the cloud values have passed through the aerosol threshold region. Measured HCl gaseous concentrations do not agree with the equilibrium predictions in the threshold region, and, in fact, continue to decrease at the same dilution rate observed for the total HCl concentrations.

In contrast to the lower cloud, the higher altitude cloud measurements are consistent with the equilibrium predictions. This segment of the exhaust cloud rose rapidly to equilibrate with the ambient air temperature at the low relative humidity (RH) observed at the higher altitudes (RH = 10-20%). Equilibrium analysis (Fig. 6) indicates that at these levels of total HCl, temperature, and relative humidity, the HCl should all be in the gaseous phase and is far removed from the aerosol threshold or transition region. The long dashed line faired through these values fits the total HCl values equally as well as the gaseous HCl concentrations. Scattering of the data measured in the higher altitude cloud segments is due to the difficulty in finding the center of this cloud since it became increasingly transparent with time and dilution. Previous measurements in Titan III exhaust clouds were not as conclusive as the results shown here because the variations in meteorological conditions did not occur at these launches.[10,11] Total HCl concentrations measured during the Shuttle ex-

periment were similar to those observed during the Titan III experiments. Gaseous HCl measurements did not agree with the prediction in Ref. 10 because the relative humidity conditions were near the aerosol/gaseous threshold. The gaseous measurements reported in Ref. 11 did agree because the relative humidity within the cloud remained well above the aerosol/gaseous HCl threshold.

Conclusions

Meteorological conditions occurring during the first Space Shuttle launch presented a unique opportunity to measure HCl partitioning between the gaseous and aerosol phases under a wide range of atmospheric relative humidities. Simultaneous measurements of gaseous and total HCl concentrations in two segments of the exhaust cloud show that an equilibrium analysis can accurately predict the HCl partitioning at stable and at very high and low relative humidities. The measurements also show that the equilibrium analysis is inadequate at the aerosol/gaseous threshold or transition region in a rapidly changing atmospheric exhaust cloud system.

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