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**DISTRIBUTIONS AND ASSOCIATIONS OF SOME OF THE CHEMICAL
ELEMENTS FOUND IN THE STRATOSPHERE*****W. A. Sedlacek and P. R. Guthals**
Los Alamos Scientific Laboratory
Los Alamos, New Mexico**Abstract**

Aerosols present in the lower stratosphere have been collected on I.P.C. filters using USAF WB-57F aircraft. The samples were examined by neutron activation analysis, scanning electron microscopy and chemical analysis (at NCAR) of water-soluble material. Studies of the collection mechanisms of the samplers and analysis of samples collected during a Sept. 1972 Lidar-Balloon-Aircraft cross-calibration experiment suggest the association of sulfate, sodium, magnesium and chlorine with particles larger than 0.2 micrometers, and nitrate and calcium with vapors or Aitken nuclei. In addition, latitudinal iodine concentration variations were measured from 75°N to 51°S on the AEC Project Airstream sampling missions in Oct. of 1972. Although the results from one set of samples can not show what effect is contributed by seasonal variations, a curious higher concentration of iodine in the Northern mid-latitudes existed during Oct. 1972. A set of samples collected in May of 1973 should show the effect of seasonal variations. Examination of tropical upwellings and thunderstorms that penetrated the tropopause gave low iodine concentrations indicating that they are probably not principle injection mechanisms. The remaining question is whether vertical diffusion and mixing across the tropopause are represented by these iodine concentrations.

1. Introduction

Under the sponsorship of the U. S. Dept. of Transportation's Climatic Impact Assessment Program (CIAP) and in conjunction with the U. S. Atomic Energy Commission's Project Airstream, Los Alamos Scientific Laboratory has been examining the aerosol burden of the lower stratosphere. The sampling is carried out by the 58th Air Weather Reconnaissance Squadron of the USAF based at Kirtland Air Force Base in Albuquerque, N. M. using WB-57F aircraft. The WB-57F will carry a scientific payload to altitudes exceeding 60,000 ft. MSL for time periods on station up to about six hours. One of these aircraft has been equipped with on-line instrumentation provided by several laboratories to record in situ H₂O vapor, O₃, NO_y, integrated IR radiation from above, integrated UV radiation, UV spectra, ion density, and inertial navigation data. Electric field measuring devices and an Aitken nuclei counter will also be used on some flights. All of the WB-57F's used for the CIAP program also collect aerosol samples. This paper will present some of the results of the analysis of these aerosol collections.

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by the U. S. Atomic Energy Commission.

II. Experiments

Two experiments will be discussed, the first is a cross calibration experiment conducted the week of Sept. 12, 1972 over Laramie, Wyoming. Balloons were launched by the University of Wyoming to measure in situ temperature, water vapor and aerosol concentration vertical profiles; a Lidar system operated by NASA Langley was used to remotely measure the aerosol vertical profile; and the WB-57F aircraft sampled the aerosols present in the lower stratosphere over Laramie.

The second experiment was a "piggy back" use of the ongoing AEC Airstream program to examine the North-South distribution of aerosols in the lower stratosphere. Airstream collections are made quarterly from 75° North to 51° South latitude at four altitudes. The flight paths are shown in Figure 1.

Figure 1. Flight Path of Project Airstream Sampling.

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present in the lower stratosphere have been collected on I.P.C. filters using USAF WB-57F aircraft. The samples were examined by neutron activation analysis, scanning electron microscopy (SEM) analysis (at NCAR) of water-soluble particles, and analysis of samples collected during the 1972 Lidar-Balloon-Aircraft cross-validation experiment suggest the association of aluminum, magnesium and chlorine with particles less than 0.2 micrometers, and nitrate with vapors or Aitken nuclei. In the latitudinal iodine concentration variation measured from 75°N to 51°S on the AEC Airstream sampling missions in Oct. of 1972, the results from one set of samples suggest that what effect is contributed by seasons, a curious higher concentration of iodine in the Northern mid-latitudes existed during 1972. A set of samples collected in May 1973 would show the effect of seasonal variation of tropical upwellings and suggest that concentrations of iodine indicated that they are principle injection mechanisms. The question is whether vertical diffusion across the tropopause are represented by the concentrations.

I. Introduction

Sponsorship of the U. S. Dept. of Energy's Climatic Impact Assessment Program and in conjunction with the U. S. Atomic Energy Commission's Project Airstream, the Los Alamos Scientific Laboratory has been examining the aerosol burden of the lower stratosphere. This is carried out by the 58th Air Weather Squadron of the USAF based at Fairchild Air Force Base in Albuquerque, N. M., using WB-57F aircraft. The WB-57F will carry a payload to altitudes exceeding 60,000 feet for periods on station up to about one hour. One of these aircraft has been equipped with instrumentation provided by the Los Alamos Laboratory to record in situ H₂O vapor, integrated IR radiation from above, infrared radiation, UV spectra, ion density, navigation data. Electric field measurements and an Aitken nuclei counter were used on some flights. All of the data for the CIAP program also collected. This paper will present some of the results of the analysis of these aerosol

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III. Equipment

Two types of samplers (U-1, LASL) are used for the aerosol collections. Figure 2 shows the locations of the samplers on the aircraft. The U-1 sampler shown in Figure 3 is a USAF design which sticks out of the bomb bay of the aircraft on the right side 55° down from horizontal. This sampler can collect up to thirteen sequential samples.

Figure 2. Location of U-1 and LASL Samplers on the WB-57F Aircraft.

Figure 3. Cross Section of the U-1 Sampler. The Numbers are the Cross-sectional Areas of the Throat and Filter in cm^2 .

The LASL sampler shown in Figure 4 is located on the wings about 41 ft. out from the center line of the aircraft. One such sampler is located on each wing, each capable of collecting a single sample per flight. An experimental modified version of the LASL sampler was also used in which a movable "cowl flap" was added to the air exit area as indicated by the dashed line in Figure 4.

This cowl flap increases the air flow through the sampler very greatly at stratospheric altitudes but also increases the tendency of large particles to collect on the upper half of the filter. This will be important as we shall see later.

Kronisol coated I.P.C. 1478 filter paper which had been pre-washed with deionized water was used to collect the aerosols.

IV. Analysis

The collected aerosol samples were examined on the filter media using scanning electron microscopy (SEM) and instrumental neutron activation analysis (INAA). Solid particles down to about 0.2 micrometers in diameter are observable by the

Figure 4. Cross Section of LASL Wing Pod Sampler. The Numbers are the Cross-sectional Areas of the Throat and Filter in cm^2 .

SEM. The principal elements present can be determined in individual particles for Z's greater than sodium by observing the fluorescent x-rays stimulated by the SEM's electron bombardment. The INAA technique senses more than thirty trace elements with varying degrees of sensitivity.

The National Center for Atmospheric Research⁽¹⁾ has examined the filters by dissolving out the water soluble material collected (at the existing concentrations) and doing chemical analysis for nitrogen as NH_3 and NO_3 , sulfur as SO_4 , sodium, potassium, calcium, magnesium, and chlorine.⁽²⁾

V. Results: Laramie Experiment

Two flights were flown on the cross calibration experiment. On the first night, collections were made with the modified LASL sampler and U-1 sampler at 59,000 ft. MSL, and on the second night, the regular LASL sampler and the U-1 sampler were used at 55,000 ft. MSL. The LASL filters were quartered and opposite quadrants were analyzed by NCAR. The entire U-1 sample was analyzed by NCAR. The results are listed in Table I.

The collection efficiency relative to isokinetic air flow has been measured for each of the samplers: for modified LASL at 59,000 ft. efficiency = 75%, for regular LASL at 55,000 ft. efficiency = 19%, for U-1 at 55,000 ft. efficiency = 47%; at the flight speeds used to make these collections. These efficiencies are for the air flow only. Although we do know that the efficiency for aerosol collection is greater than each of these due to the ballistic paths of particles crossing lines of air flow, we have no direct way of measuring the aerosol collection efficiency at altitude.

Not only will the aerosol collection efficiency vary as a function of aircraft velocity and altitude (air density), but it will also be a function of the diameter and density of the aerosol particles. We also know from low altitude studies of

Table I

µgm

Type	N as NO ₃ ⁻	SO ₄ ⁼	Cl ⁻	Ca ⁺⁺	Mg ⁺⁺	Na ⁺
Modified LASL upper outside 1/4	1459	2119	169	467	115	340
59K ft. MSL lower inside 1/4	1386	1031	51	364	68	23
Total	2845	3150	220	831	183	363
U-1 #5 55K ft. MSL	525.9	313.5	10.5	147.5	21.0	2.1

the samplers in power plant plumes that patterns of large particle deposition are observed which are dependent on the aircraft velocity and angle of attack. These effects will be even more pronounced in the much thinner air of stratospheric altitudes. These effects are also greater with the higher efficiency modified LASL sampler.

Let us then consider the relative amounts of material collected (see Table I) independently of knowledge of the absolute collection efficiencies. Similar size and density particles should deposit in similar patterns. First, observe the collection made with the modified LASL sampler. Note that the amounts of SO₄⁼, Cl⁻, Na⁺, and Mg⁺⁺ deposited on the upper portion of the filter are approximately twice as great as the amounts on the lower portion of the filter. However, the distributions of NO₃⁻ and Ca⁺⁺ are nearly equal on the two filter portions.

Similarly, if one compares the ratios of the total amounts of NO₃⁻ and Ca⁺⁺ collected by the modified LASL sampler to that collected by the U-1, they are both approximately 5.5. However, the same ratios for SO₄⁼, Cl⁻, Mg⁺⁺, and Na⁺ are all much higher.

Although these data are from a single experiment which reflects the composition of a particular location in the stratosphere at a particular time, they seem to suggest that NO₃⁻ and Ca⁺⁺ behave similarly. To go one step further, sampling with polystyrene filters and I.P.C. filters by NCAR as previously reported, together with laboratory experiments indicating the absorption of HNO₃ vapor on I.P.C. but not on polystyrene lead to the conclusion that the NO₃⁻ observed in the stratosphere was probably in the vapor state.⁽³⁾ The lidar and balloon experimenters reported observations of about one and two particles per cubic centimeter having diameters greater than 0.5 micrometers and 0.25 micrometers respectively. No such particles were observed on the filters although an amount of sulfate was found equivalent to the observed particle counts if a density of about 1.5, mass median diameter of 0.5 micrometers and composition of H₂SO₄ is assumed. SO₂ does not absorb on the klonisol coated I.P.C. filter paper.⁽⁴⁾ Since a liquid droplet impacting on the filter at the collection velocity of over 2,000 ft/min would be expected to break into many small droplets and be absorbed by the filter fibers, we conclude that the

majority of the particles greater than 0.25 micrometers are probably droplets of sulfuric acid and/or sulfuric acid solutions of other salts at the time of this experiment.

Although it is difficult to imagine calcium existing in a vapor form in the stratosphere, very small Aitken nuclei would be expected to behave quite similarly to a vapor under our sampling conditions. We therefore conclude that the calcium probably resides principally in the ultra small Aitken nuclei which would not have been observed by the lidar or the balloon.

VI. Results: Oct. 1973 Airstream Collections

Stratospheric aerosol collections were made on the high altitude halves of selected Oct. 1972 Airstream sampling missions as indicated by Figure 5. Collections were not made on all Airstream

Figure 5. Oct. 1972 Project Airstream Flights Profile. The Numbers are Nanograms per cubic meter of Ambient Air Average for those Flights where LASL Samplers were used.

flights due to aircraft operational constraints. Of particular interest is the distribution of iodine. Note the higher concentrations present in the Northern mid-latitudes at the lower stratospheric altitudes. A second series of Airstream

flights scheduled for April was delayed due to aircraft mechanical problems and therefore the conjugate set of data is not presently available. Without this data to indicate the seasonal variations of stratospheric iodine concentrations, it is difficult to propose a model for the mechanisms which establish the observed distribution. Examination of a thunderstorm with an iodine concentration around and over the top of 0.068 nanograms per cubic meter at 45,000 to 56,000 ft. and of two tropical upwellings in the ITCZ region having concentrations of 0.055 and 0.080 over them at 55,000 to 60,000 ft. indicate that these large storms penetrating the tropopause probably do not carry large amounts of iodine into the lower stratosphere. Therefore, the question still remains, could these iodine concentrations represent the vertical transport by diffusion and mixing across the tropopause of air carrying very small particles or vapors containing iodine, possibly coming from the more heavily industrialized Northern mid-latitudes?

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