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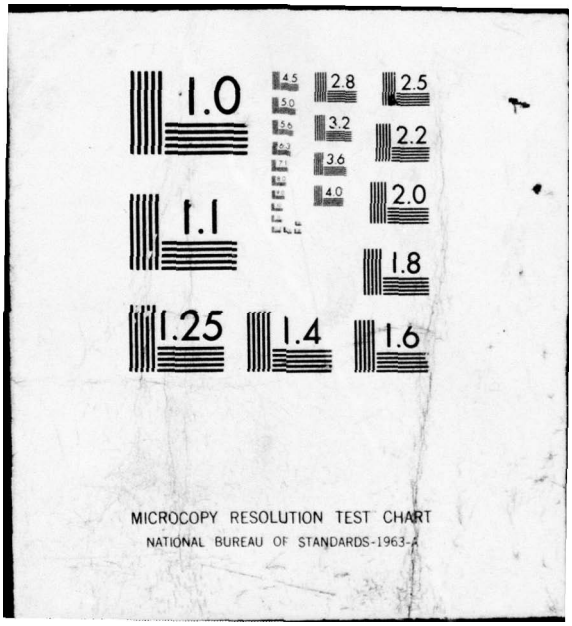
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REPORT NO. 1941

(Supersedes IMR Nos. 192, 324, 424 and 442)

FINAL REPORT ON BALLOON-BORNE, MASS-SPECTROMETER PACKAGE FOR STUDYING STRATOSPHERIC POSITIVE IONS AND NEUTRAL MOLECULES

George E. Keller

October 1976

USA BALLISTIC RESEARCH LABORATORIES
ABERDEEN PROVING GROUND, MARYLAND

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A balloon-borne, mass-spectrometer package for studying stratospheric positive ions and neutral molecules was built for the BRL by personnel of the University of Denver. The package was flown three times with limited success. Stratospheric ions were not definitely detected on any flight, but data acquired on the third flight showed that the concept of particle sampling with a very clean balloon package was sound. The package was destroyed at the end of the third flight following a free fall from 30 km.

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I. INTRODUCTION

The performance of communications systems, radars, and other defense systems is predicted using phenomenology codes which employ simplified chemistry. Extensive chemical codes of the lower ionosphere have been developed in our laboratory to check the reliability of the simplified chemistry. The development of these large chemical codes requires both laboratory measurements of relevant reaction rate coefficients and *in situ* measurements of ionic- and neutral-constituent densities in the lower ionosphere. The balloon-borne mass spectrometer described in this report was used for the first BRL effort to determine the distributions of mass-identified positive ions in the stratosphere.

There have been several stratospheric measurements which have yielded the total positive ion number density as a function of altitude. Rose and Widdel[1] deduced a density of about 7×10^2 positive ions per cm^3 at 40 km. Several measurements by Mitchell *et al.*[2] suggested that there are 5 to 15×10^3 positive ions per cm^3 at 40 km. Bragin[3] found about 3×10^3 positive ions per cm^3 at 40 km. Hake[4] analyzed several measurements and deduced an "average" profile which extrapolates to about 10^5 positive ions per cm^3 at 40 km. None of these research efforts identified the ions involved, however. Very recent work by Croskey,[5] who flew a Gerdien condenser probe in the mesosphere and stratosphere, showed that there was a great deal of fine structure in the mobility data. He attributed this to the presence of various hydrated positive ions or ion families.

To this date, the only reported stratospheric measurement which identified the ions is by Krankowsky and Arnold.[6] One of their rocket-borne instruments operated down to 35 km and identified masses of 37 and

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[1] G. Rose and H. U. Widdel, "Results of concentration and mobility measurements for positively and negatively charged particles taken between 85 and 22 km in sounding rocket experiments," Radio Science 7, 81 (1972).

[2] J. D. Mitchell, L. C. Hale, R. O. Olson, J. Randhawa, and R. Rubio, "Positive Ions and the Winter Anomaly," Radio Science 7, 175 (1972).

[3] Bragin, Yu. A., "Direct Measurements of Ion and Electron Concentration in the Stratosphere and the Mesosphere," in Space Research VII, R. Smith-Rose, ed., p. 391 (North-Holland Publishing Company, Amsterdam, 1967).

[4] R. D. Hake, Jr., E. T. Pierce, and W. Viezee, "Stratospheric Electricity," Stanford Research Institute report on SRI Project 1724, Jan 73.

[5] C. Croskey, "In Situ Measurements of the Mesosphere and Stratosphere," Penn. State Univ. Report No. PSU-IRL-SCI-442, 1976.

[6] D. Krankowsky and F. Arnold, "The Nature of Stratospheric Positive Ions," presented at the XVII Meeting of COSPAR, International Symposium on Solar-Terrestrial Physics, Sao Paulo, Brazil, 1974.

55 amu and lesser amounts of 60±2 and 80±2 amu. The first two ions were identified as hydrated protons; the identity of the second two ions is still unknown. Two other groups are known to be developing ionic balloon-borne mass spectrometers. R. O. Woods at Sandia Laboratories[7,8] has made three balloon-borne mass spectrometer measuring flights, but he has not published any conclusive ion data from them. A group headed by E. Arijs at the Belgian Institute of Space Aeronomy has likewise had several flights of a balloon-borne mass spectrometer, but technical difficulties have thus far prevented successful measurements.[9,10] Two papers document some of the details of the Belgian apparatus.

Balloon-borne mass spectrometers can also be used to measure neutral molecules in the stratosphere. Narcisi *et al.* made neutral composition measurements up to an altitude of 28 km with a time-of-flight mass spectrometer.[11] Woods obtained neutral mass spectra as a part of his measurement effort;[8] one of his spectra is shown in Section VII of this report. Aikin and Maier are developing a photoionization mass spectrometer package which may be employed in NO_x studies.[12]

Our calculations, based on the work of Kebarle,[13] predict that the dominant positive ion at 40 km will be $H^+(H_2O)_4$ (mass 73), with smaller concentrations. These calculations assume a "dry" stratosphere, i.e., a mixing ratio of water vapor of 4 ppmv. Some water vapor measurements in the stratosphere have suggested that the mixing ratio of water actually increases above the tropopause. If that were true, the ion distribution would be shifted to larger masses. If there were an

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[7] R. O. Woods and T. K. Devlin, "A cryopumping system for balloon-borne mass spectrometers," Rev. Sci. Instrum. 45, 136 (1974).

[8] R. O. Woods, "Mass Spectrometer Data," Chapter 12 in "Stratospheric Composition Balloon-Borne Experiment - 18 September 1972," compiled by H. N. Ballard and F. P. Hudson, ECOM-5554, Jan 1975.

[9] E. Arijs, "Effusion of ions through small holes," Vacuum 24, 341 (1974).

[10] E. Arijs and D. Nevejans, "Programmable control unit for a balloon-borne quadrupole mass spectrometer," Rev. Sci. Instrum. 46, 1010 (1975).

[11] R. S. Narcisi, R. A. Langley, H. A. Cohen, and J. M. Elwell, "Balloon-Borne Mass Spectrometer Measurements of the Constituents of the Atmosphere to 28 Kilometers," AFCRL-66-339, May 1966.

[12] A. C. Aikin, personal communication.

[13] P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, "The Solvation of the Hydrogen Ion by Water Molecules in the Gas Phase. Heats and Entropies of Solvation of Individual Reactions: $H^+(H_2O)_{n-1} + H_2O \rightarrow H^+(H_2O)_n$," J. Am. Chem. Soc. 89, 6393 (1967).

appreciable concentration of ammonia in the stratosphere,[14] the work of Payzant *et al.*,[15] Fehsenfeld and Ferguson,[16] and Kadlecek[17] implies that the stratospheric ions would then be of the form $NH_4^+(NH_3)_n(H_2O)_m$.

The beginning of the BRL effort dates to a meeting at El Paso, Texas, on 22 Apr 71, where representatives of BRL, ASL, UTEP, Sandia Laboratories, ARO and USAMC met to discuss the need for balloon-borne mass spectrometer sampling of the sub-D region of the ionosphere. Priorities for the measurements were established, and cooperation and funding were discussed. A lack of funding caused a subsequent long delay in the start of the program, but many of the ideas discussed in that early meeting were reflected in the mass spectrometer package reported here.

A contract was let in November of 1972 with the University of Denver to build the package. The package underwent several changes from the initial plans before it was first taken to the field. For example, at first there was a very strict weight limit, but that was relaxed when a decision was made to fly at 40 km rather than 45 - 50 km. The details which follow describe the package as it flew.

II. THE PACKAGE

A detailed BRL Contract Report[17] documents the design and construction of the mass spectrometer package. Thus the equipment descriptions in this report will be brief.

A. The Mass Spectrometer. The radio-frequency, quadrupole mass spectrometer incorporated 6.35 mm diameter, 140 mm long, molybdenum rods and and electron-impact ionizer manufactured by the Finnigan Instruments Corporation. The detector was a twenty-stage multiplier manufactured by Johnston Laboratories. The RF/DC generator which drives the rods was entirely solid state. The entire mass range, 1 - 150 amu, was covered in one continuous sweep with a resolution that could be set to be better than one amu. When ambient positive ions were being studied, the ions were individually counted. When ambient neutrals were being studied, the ions of the neutrals were individually counted and their current measured on alternate scans of the spectrometer.

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[14] J. D. Payzant, A. J. Cunningham, and P. Kebarle, "Gas Phase Solvation of the Ammonium Ion by NH_3 and H_2O and Stabilities of Mixed Clusters $NH_4^+(NH_3)_n(H_2O)_w$," Can. J. Chem. 51, 3242 (1973).

[15] F. C. Fehsenfeld and E. E. Ferguson, "Thermal energy positive ion reactions in a wet atmosphere containing ammonia," J. Chem. Phys. 59, 6272 (1973).

[16] J. A. Kadlecek, "Ion molecule reactions of atmospheric importance," Interim Report to NSF. Atmospheric Sciences Research Center, State University of N.Y. - Albany, Publ. No. 263, 1974.

[17] D. G. Murcray and R. C. Amme, "Construction of a Balloon-Borne RF Quadrupole Mass Spectrometer Package," BRL Contract Report No. 235, 1975. This report is available as AD A011 313.

B. The Valved Aperture System. This system uncovered the 100 μm-diameter aperture for straight-through entrance of the ions and neutrals to be studied. The seal consisted of a tiny polyimide disk with a raised edge and the tungsten carbide aperture plate. The covering and uncovering were electrically actuated. The aperture was open for about 6 seconds for a neutral molecule mass spectrometer operation and for about 12 seconds for a positive ion operation. The potential on the aperture could be set from the ground to be any one of five values between 0.0V and -20.0V to help overcome possible package charging (see Appendix). A schematic view of the sampling arrangement is shown in Figure 1.

Calculations of the aperture size needed were based on the stratospheric pressure, the pressure needed for the mass spectrometer, and the pumping speed available. It was assumed, lacking data, that between 10% and 50% of the ions contained in the sampled air would get through the aperture and into the mass spectrometer. This estimate seems to have been far too large, as will be discussed in a later section of this report.

C. Pumps. The principal pumping was accomplished with two titanium sublimation pumps, which were started a few seconds before the aperture was valved open and turned off when the aperture was closed. A small liquid helium cryopump assured that the noble gases were well pumped. A small VacIon appendage pump also operated continuously, backing up the other pumps as well as providing a measurement of the pressure in the vacuum chamber.

D. Vacuum Chamber. The vacuum chamber was constructed of stainless steel with metal seals. Well-baked and pumped, its ultimate pressure was on the 10^{-7} Pa (10^{-9} Torr) range. When the aperture was open, and the pressure was 267 Pa (2 Torr) on the outside of the vacuum chamber, the measured pressure in the vacuum chamber was about 2×10^{-3} Pa (1.5×10^{-5} Torr). A schematic view of the vacuum portion of the package is shown in Figure 2. A is the aperture cover, B is the aperture plate, C is the quadrupole mass spectrometer, D is the detector, E represents a titanium sublimation pump, F and G are shields to keep titanium off the mass spectrometer, H is the liquid helium cryopump, and J is the VacIon appendage pump.

E. Temperature. Temperature sensors for measuring the ambient temperature of the stratosphere were supplied by the Atmospheric Sciences Laboratory of White Sands Missile Range. The sensors consisted of bead thermistors embedded in thin mylar film. The technique for their use is described by Ballard and Rofe.[18]

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[18] H. N. Ballard and B. Rofe, "The Thermistor Measurement of Temperature in the 30-65 km Atmospheric Region," Stratospheric Circulation, Vol. 22, Progress Series American Inst. of Aeronautics and Astronautics, New York, Academic Press, p. 141, 1969.

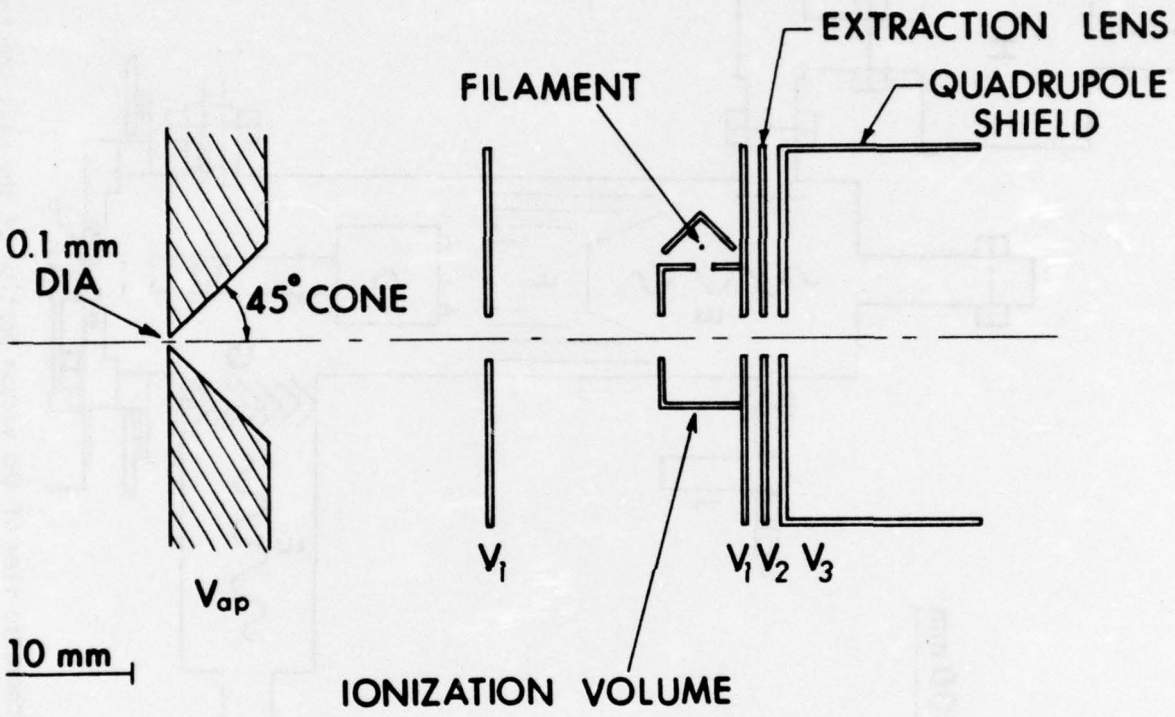

Figure 1. Schematic view of the sampling arrangement.

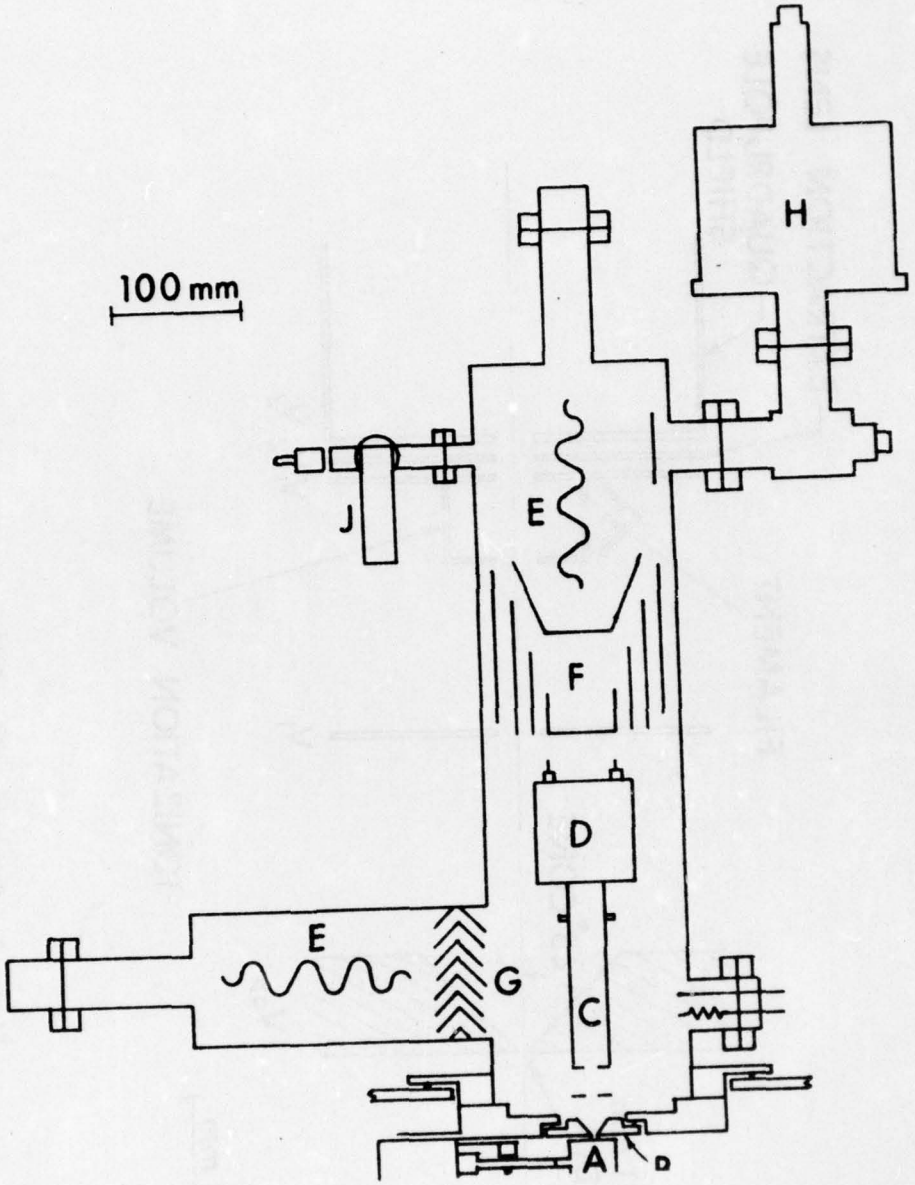

Figure 2. Schematic view of the vacuum portion of the mass spectrometer package.

F. Pressure. The ambient pressure of the stratosphere was measured by three Rosemont pressure transducers supplied by the National Scientific Balloon Facility.

G. Cosmic Ray Ionization. A Neher-type cosmic-ray-ionization chamber[19] was used for measurements of the volume ionization of the stratosphere.

H. Tape Recorder. There was an on-board 7-track digital tape recorder in the package which served as the primary data storage device. The recorder used standard-size reels of tape.

I. Control Circuitry. On-board, all-solid-state control circuitry controled the operation of the parts of the package. Housekeeping data were assembled each minute and sent to the on-board tape recorder and to the TM encoder. Mass spectrometer operations could be commanded from the ground or from an on-board, pre-programmed storage register which was controlled by an on-board clock. Mass spectrometer scan operations over the mass range could be commanded from either source; fixed-peak operations could be commanded from the ground. The heating of the titanium pumps limited these operations to a frequency of one every 5 minutes. The pumping could tolerate an outside pressure of up to about 1.3×10^{3} Pa (10 Torr), which occurs at altitudes above about 30 km.

J. The Gondola. The gondola was a stainless steel box with dimensions 890 x 890 x 660 mm. By the time of its second flight, all of the sides of the gondola were coated with a smooth, hard, low-outgassing white epoxy paint to aid heat dissipation from the titanium sublimation pumps. All of the experiments except the temperature sensors, UV detector, and cosmic-ray ionization chamber were contained within the gondola for the sake of cleanliness. No tape, or cardboard, or other "normal" ballooning materials were permitted on the outside of the gondola. Collapsible, stainless steel, energy-absorbing legs and a stainless steel screen well below the gondola provided landing protection for the gondola and reduced effects from possible package charging (see Appendix).

K. Real Time Data Analysis. A real time data analysis program for the PDP-11/20 computer at the National Scientific Balloon Facility (NSBF) was written by BRL personnel and was improved by University of Denver personnel. The program provided a print of the housekeeping data each minute and the mass spectra just following each mass spectrometer operation. This was an especially difficult program to write, for all data manipulations had to take place in the 222 μsec intervals between data word transmissions.

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[19] H. V. Neher, "An Automatic Ionization Chamber," Rev. Sci. Instrum. 24, 99 (1953).

III. FIRST ATTEMPT TO FLY

The package was first taken to the NSBF at Palestine, Texas for flight preparation in June of 1974. The package arrived at the NSBF on 5 June. We planned to do final tests of all of its components, install telemetry electronics, check the telemetry link, and fly the package before the NSBF annual 2-week vacation which began on 22 June. In fact, difficulties inside the main spectrometer vacuum system forced us to open it three times. Each of these operations consumed several days with the removal of the vacuum system from the package, opening the vacuum system, repairing it, closing it, pumping and baking it, and reinstalling it in the package.

The first difficulty was a dead short across the rf leads to the spectrometer. We found that it was caused by a small piece of titanium filament, which presumably lodged in a baffle after a filament failure several months ago and fell out of the baffle during the transit of the package. While the vacuum system was open, a freshly rejuvenated electron multiplier detector was installed.

The second difficulty was an extra 30 pF load across the rf leads. The load disappeared while the spectrometer was being carefully examined, and it could not be made to return.

The third difficulty was that the gain of the freshly rejuvenated electron multiplier detector was too low by a factor of 10^4 - 10^6. A new multiplier was flown in from Maryland and installed. When the new multiplier failed to work *at all*, we decided that the contractor should take the package back to Denver to be repaired in a less hostile environment.

There were some positive effects of the first visit to the NSBF with the package. Launch personnel there had an opportunity to see the package and discuss with us the special handling it would require. Rigging for the launch and the actual launch techniques were discussed and agreed on.

Soon after the package arrived back in Denver, it was discovered that the main signal lead from the detector was broken, presumably during the final installation of the second fresh multiplier.

IV. FIRST FLIGHT

A. Preparation. The package left again for Palestine on 21 Aug 74. The construction of the telemetry (TM) package by NSBF personnel started soon after its arrival. One slowdown in the preparation was caused by a programmable read-only memory (PROM) which had been programmed incorrectly at the factory. Several days were spent checking the package data handling and data transmission with the data receiving equipment and real-time data analysis program. The package was ready to fly on 13 Sep 74.

B. The Flight. A long period of bad weather delayed the launch for weeks. The package was finally launched at 0130 CDT on 1 Oct 74. The mass of the package was 287 kg at the time of the launch. The main balloon had a volume of 3.29×10^5 m^3 (11.62×10^6 ft^3). A 300 m (1000 ft), 4.5×10^4 N (10,000 lb) test nylon cord separated the parachute, NSBF electronics, and balloon from the clean gondola. A 496 m^3 (17,000 ft^3) tow balloon was used to assist in the initial launch of the package. The tow balloon was cut cleanly off at about 1500 m (5000 ft) altitude. The balloon ascended to a float altitude of about 40 km in approximately 2 1/2 hours. The path of the flight was almost due south from Palestine. Cut-down was initiated at 0830 CDT, and the gondola impacted near Huntsville, Texas. The package was recovered in excellent condition and returned the same day to the NSBF.

C. Results. The new launch pad at the NSBF is not in line of sight with the control tower, so the TM signal was too weak to do full scale tests on the launch pad.

At about 15 km, several problems arose. Some of them are still not completely explained. The housekeeping data show that starting then there were a number of "ground-commanded" positive-ion, fixed-peak mass spectrometer operations. These operations popped up continually until cut-down. There could have been a correlation with the outside temperature, for that was about the tropopause, whose temperature that day was quoted at about 200 K (-73°C). Indeed the temperature sensors showed that the start of the problems came at the coldest temperature encountered on the flight. There were no ground commands of any kind at that time; the on-board program was checked later and found to be correct, that is, asking for no operations at that time. The difficulty was more than just a burst of noise, or a series of noise pulses, for the fixed peak sample number "commanded" was 1777 octal, which is 1 111 111 111 binary, a number hardly likely to result from noise. The result of these extra operations was that the pumps were overwhelmed, the pump batteries overheated and at least one "boiled over," and no real mass spectrometer data could be taken on this flight. The extra heat caused problems with the pressure transducers and with the main TM unit, which failed just before cut-down.

The problems at 15 km would have been easier to diagnose if the on-board tape recorder had not also had a problem early in the flight, probably even before the launch. The collapsible legs did not function as designed, but they did sacrifice themselves for the major package. The UV detector and the cosmic ray ionization chamber seem to have worked as designed, as far as one could determine from the limited real-time data. The real-time data analysis program worked as planned, and it afforded a graphic display of a flight in trouble. The high voltage lead to the multiplier detector arced to ground at some time during the flight. This may well have saved the detector, for it could have been destroyed by arcing inside the vacuum chamber when the inside pressure was so high. The analog data values which are transmitted in the housekeeping data transmission became scrambled at 0235 CDT.

D. Restoration. The next several months were spent restoring the package to flight status. A modest redesign of the tape recorder solved its problems. After much discussion a change in the method of leg attachment was agreed on. Several aperture plates were tried while attempting to sample thermal ions in laboratory tests. Instead of the expected 10% to 50% sampling efficiency, thermal ions were found to be admitted with about an 0.1% efficiency, remarkably independent of the design of the aperture plate. These tests did not reach a satisfactory, unambiguous conclusion before all of the other parts of the package were ready and we decided to fly the package again. This phase of the program was slowed down by severe limitations imposed on the travel of the author of this report, starting in January 1975.

V. SECOND FLIGHT

A. Preparation. The package was taken to the NSBF again on 19 June 1975. It was unpacked and testing was begun on 20 June. Tests were completed on the package proper and the up-link TM on Saturday, 21 June. The down-link TM box was finally received from NSBF electronics personnel on Thursday evening, 26 June. The entire assembly was tested that weekend, including a full-scale environmental check. The environmental test was performed with the sides and insulation removed from the gondola box. The test chamber was pumped to a pressure corresponding to the tropopause, cooled to below -10°C, and held there for more than a half hour. Then the chamber was pumped to less than 250 Pa (1.87 Torr). After a few minutes, the temperature was increased to +30°C and those conditions were maintained 8 hours before removing the mass spectrometer package from the chamber. The package performed flawlessly during all of these tests. All of the tests were completed by Tuesday morning, 1 July 1975. The first attempt to fly the package came on Saturday, 5 July. A morning launch had been decided on to make the launch easier and minimize waiting at the NSBF for weather. The flight attempt on 5 July had to be canceled when condensation of the morning fog on and inside the package caused control circuitry difficulties.

B. The Flight. The package was launched at 0630 CDT on 7 July 1975, by the NSBF personnel. The mass of the package was 287 kg at the time of the launch. The main balloon had a volume of 3.29×10^5 m^3 (11.62×10^6 ft^3). A 300 m (1000 ft), 4.5×10^4 N (10,000 lb) test nylon cord separated the parachute, NSBF electronics, and balloon from the clean gondola. A 496 m^3 (17,000 ft^3) tow balloon was used to assist in the initial launch of the package. The tow balloon was cut cleanly off at about 1500 m (5000 ft) altitude. The balloon ascended to a float altitude of about 40 km in approximately 2 1/2 hours. The path of the flight was almost due west from Palestine. Cut-down was initiated at about 1215 CDT by the chase airplane, and the gondola impacted just west of Midland, Texas. The package was recovered in excellent condition and was taken by truck directly back to Denver, Colorado for repairs.

C. Results. At about 23.8 km a malfunction of the control circuitry caused the valved aperture to open and stay open. Since it did not open as a part of a sampling operation, the pumps did not turn on, nor could they be turned on without initiating a complete sampling operation. If the real difficulty had been only a faulty aperture status indication on the ground, such an operation would have damaged the spectrometer for the remainder of the flight. Shortly before the package had risen to float altitude, two positive ion sampling operations were commanded, with the hope that the valve closing signals at the end of the operations would close the valved aperture and save the flight. The effort was unsuccessful. When the package had reached float altitude, a neutral molecule sampling operation was commanded. Mass spectrometer data were obtained and recorded on the onboard tape. At the end of the operation, the valved aperture closed - never to open again - for later the open solenoid was found to have finally burned out. As soon as the valve closed, the pumps brought the pressure in the vacuum system down quickly, indicating that the pumps can survive considerable overloads. The remainder of the flight time was used to check the onboard and ground command circuits to verify that they worked correctly.

The mass spectrometer data which were obtained could not be interpreted quantitatively due to the high pressure (4×10^{-2} Pa maximum) in the mass spectrometer vacuum chamber. However, the data were quite different from test data in that the peak at m/e = 18 due to water could not be found. There were large peaks at 14, 16, 20, 28, 32, 40, and 44 as expected. Since an overriding consideration in the design, construction, and flight of this package has been the minimization of sources of water carried aloft, the initial finding of very small water content in the sampled stratospheric air was most gratifying.

The cosmic ray ionization chamber stopped working after all tests were completed but before the flight. Fixing it would have delayed the flight, so it was disconnected for the flight. The temperature sensors both worked well. Their variations showed that the package either swung or rotated or both during most of the flight. The absolute value of the readings was too warm, suggesting that the sensors were mounted too close to the warm gondola. The onboard tape recorder worked well. There may have been some high voltage arcing which occurred after the valve opening, for noise affected some of the control circuits. The collapsible legs did not function as designed, but they did sacrifice themselves for the major package. The real time data analysis program worked as planned, and it again was an invaluable aid in determining what was going wrong (and right) with the flight. The UV detector worked as designed.

VI. THIRD FLIGHT

A. Preparation. The package was returned to Palestine on 2 September 1975. The telemetry package was constructed by NSBF personnel and delivered on Friday afternoon, 5 September. Preliminary tests on Saturday, 6 September, showed that the package was in good condition. A full-fledged environmental test was made on Sunday, 7 September. The on-board tape recording of the environmental chamber test was examined in detail on Monday, 8 September. There were a few unexplained difficulties as the package got quite hot toward the end of that test. We decided to pack the package as if to fly it and then to turn it on and watch its operation as it heated up. The package performed flawlessly for 10 hours on Tuesday, 9 September.

There were six attempts at a morning flight of this package on this trip:

1) 11 Sep - scrubbed due to high winds.

2) 16 Sep - scrubbed due to heavy rains.

3) 17 Sep - scrubbed when rope between package and tow balloon broke, launching the tow balloon without the package.

4) 18 Sep - scrubbed due to high winds.

5) 19 Sep - scrubbed due to high winds.

6) 21 Sep - flight.

B. The Flight. The package was finally launched at 0748 on 21 September 1975 by the NSBF personnel. The mass of the package was 245 kg at the time of the launch. The main balloon had a volume of 3.3×10^5 m^3 (11.6×10^6 ft^3). A 300 m, 4.5×10^4 N (10,000 lb.) test nylon line separated the parachute, NSBF electronics, and balloon from the clean gondola. A 500 m^3 tow balloon was used to assist in the initial launch of the package. The wind at the time of launch was 6-8 knots, gusting to 10 knots, but the launch, while spectacular, was never in doubt. The tow balloon was cut cleanly off at about 1500 m altitude. The balloon ascended to a float altitude of 40 km in approximately 2 1/2 hours. The path of the flight during the 5 1/2 hours of data gathering was south and a little west from Palestine. At 1530 the flight was turned over to NSBF personnel for cutdown.

There were two entirely separate mechanisms for firing squibs to separate the balloon from the parachute, permitting the packages to descend. NSBF first tried the two command cut-down frequencies, both from the control tower and from the chase airplane. These circuits had been demonstrated to work by command from the airplane while the package

was on the launch pad. Neither transmitter could cause cut-down signals on either frequency to effect cut-down. There was also a clock cut-down device on board, set for about 1600. All of its parts, including batteries and wires, were separated from the command cutdown. The clock cut-down device also failed to effect cut-down. There followed a very difficult evening during which NSBF personnel tried all the techniques they could imagine, including sending out a back-up airplane with another command transmitter and varying the cut-down command frequencies somewhat. None of these efforts succeeded. By midnight the helium had cooled enough that the balloon had settled down to about 30 km, where the winds were about 40 knots from about 80°. The package passed San Antonio and headed for Del Rio, Mexico, and the Pacific beyond. When it became clear that the flight would cross an international border and would eventually be lost in the Pacific, NSBF personnel decided to cut the package below the parachute. They did that at about 0400 on 22 September, and the package free fell from 30 km. The package landed just 6.5 miles from the Mexican border. While the package was demolished, the onboard data tape was recovered in good condition.

C. Results. On this third flight, there were 21 successful sampling operations. Neutral molecules were scanned 7 times, 8 positive ion mass spectra were made from 0 - 150 amu, and positive ion fixed peak operations corresponding to masses 55, 73, 91, and 109 were obtained in an attempt to detect $H^+(H_2O)_n$ ions. No mass peaks were seen in the positive ion scan data. The fixed peak counting rates for positive ions of masses 55,73, and 91 were slightly higher than the background counting rate of 4.2 counts per second, but not enough higher to conclude that these ions were detected. This apparent low sensitivity to thermal ions agrees with the laboratory tests which had been performed with this system. The effect of this finding is discussed in Section VIII. The neutral data were carefully examined for evidence of water carried aloft. There was none detected; the data are discussed in detail in Section VII.

Again on this flight there was considerable fading in and out of the down-link telemetry signal. The experiment worked well enough and stayed up long enough on this flight that the problems could be examined in some detail. We agreed after the flight that the problems were caused by package rotation on the long load line and multipath reflections off the protective screen below the package. With this understanding, flights of future packages should have much improved data telemetry. It should be emphasized that this communications problem is entirely different and separated from the cut-down problem.

The cosmic ray ionization chamber worked during the first few minutes of the flight, but then its output began to vary widely. Since its output should have been quite constant at float altitude, the data are not believed to represent real ionization due to cosmic rays. One of the builders of this instrument, P. R. Williamson, believes that temperature variations caused both electronics instability and mechanical flexing, which caused the erratic data.

The temperature sensors both worked well. Their variations showed that the package either swung or rotated or both during most of the flight. The absolute value of the readings was too warm, suggesting that the sensors were mounted too close to the warm gondola or that they were mounted too close to the telemetry antenna and were affected by its radio-frequency radiations.

VII. NEUTRAL MOLECULE RESULTS

There were 7 successful neutral molecule scanning operations on the 21 Sep 75 flight. Each operation consisted of 5 count-current pairs of mass spectra with the valved aperture open. Taking into account slow valve openings and other minor problems, there were 27 excellent count-mode scans and 32 excellent current-mode scans. This section is devoted to using those data to establish the sensitivity of the mass spectrometer to neutral molecules.

One would expect a N_2^{28}/O_2^{32} peak-height ratio of 3.72/1 in a well-mixed standard atmosphere. Figure 3 establishes that the peak due to O_2 is 2.24 times smaller than it should be (perhaps due to source reactions). One would expect a N_2^{28}/Ar^{40} peak-height ratio of 83.3/1 in a well-mixed standard atmosphere. From Figure 3 one finds that the peak due to Ar is 7 times too tall (probably because the titanium sublimation pumps didn't pump the Ar as efficiently as N_2, and the cryopump had a much smaller pumping speed). There is no evidence of a peak due to H_2O, which should have fallen at sample number 90.

The 27 count scans are combined in Figure 4, which shows again the absence of the m/e = 18 peak. Note that the m/e = 28, 32, and 40 peaks produced saturation count rates, so we must scale small peaks from some other feature.

If one assumes that the peak at m/e = 34 is due to, and due only to, oxygen isotopes, and that the peak at m/e = 36 is due entirely to the argon isotope, one can deduce the sensitivity of the instrument. We define sensitivity as a signal-to-noise ratio of one-to-one, where one should be "just able" to detect the signal from a minor neutral constituent.

Figure 5 is a detail of the water area. Note the background level before and after the peaks and the uncertainty of the determination of the background at m/e = 18. We will use the uncertainty at m/e = 18 as the noise in our sensitivity calculations.

Figure 6 is a detail of the oxygen and argon isotope area. If one scales the difference between the m/e = 34 peak height and the background level, multiplies it by 2.24 (because an oxygen peak will be smaller by that amount), assumes it is due to a gas with a volume mixing ratio of

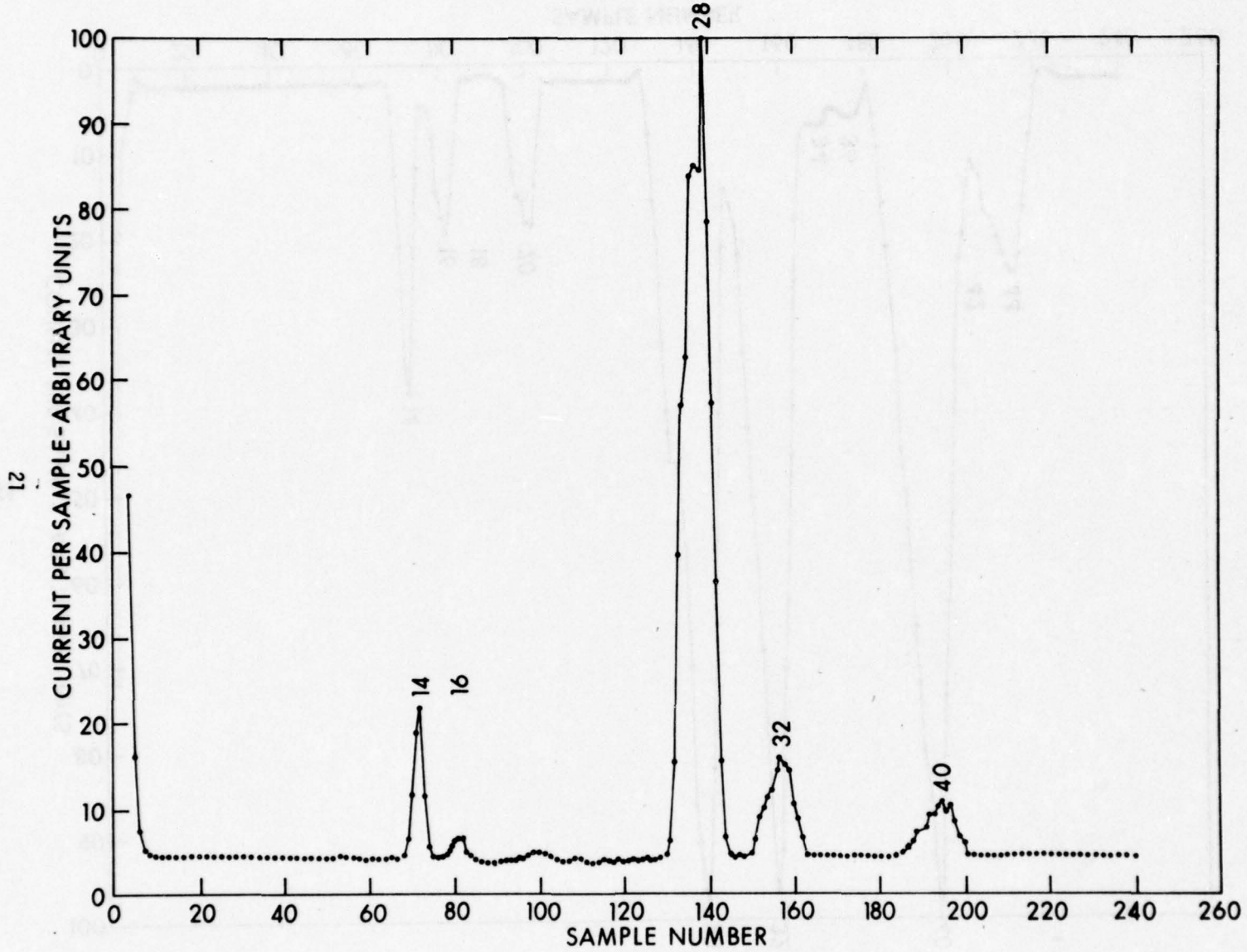

Figure 3. The sum of 32 current-mode scans.

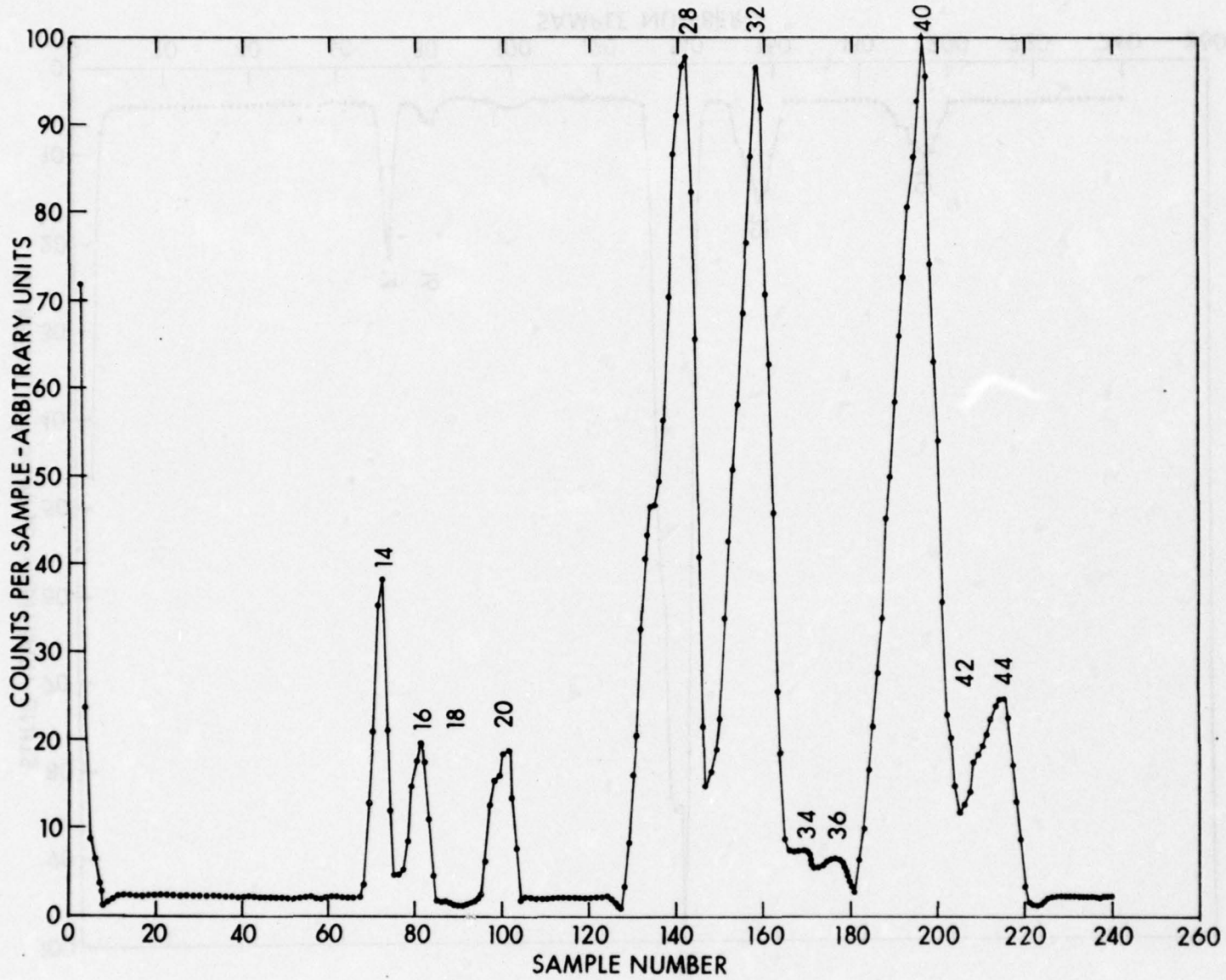

Figure 4. The sum of 27 count-mode scans.

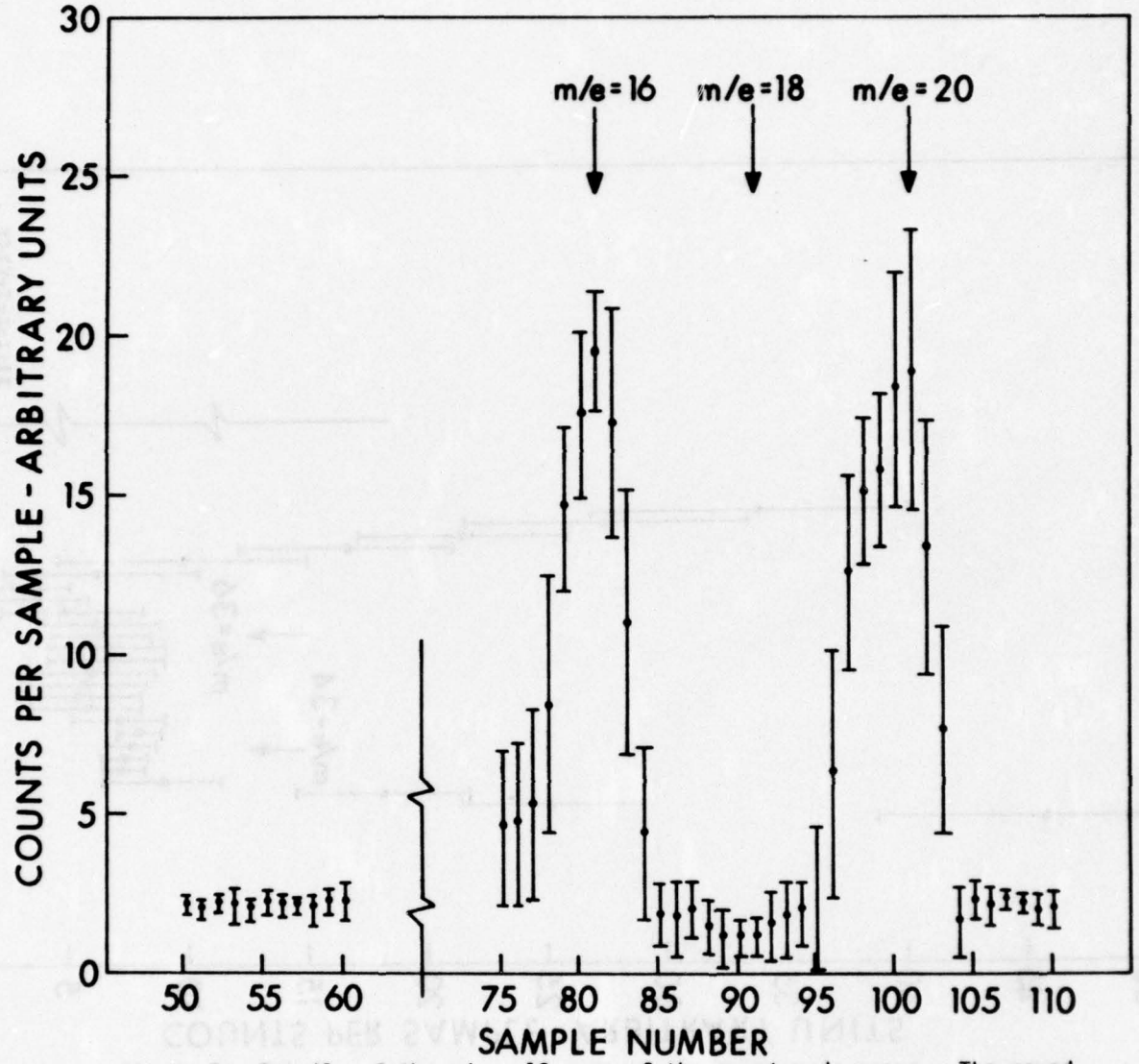

Figure 5. Details of the m/e = 18 area of the count mode scans. The round dots denote the mean count rate at each sample point; the error bars show the uncertainty of the determination of each mean.

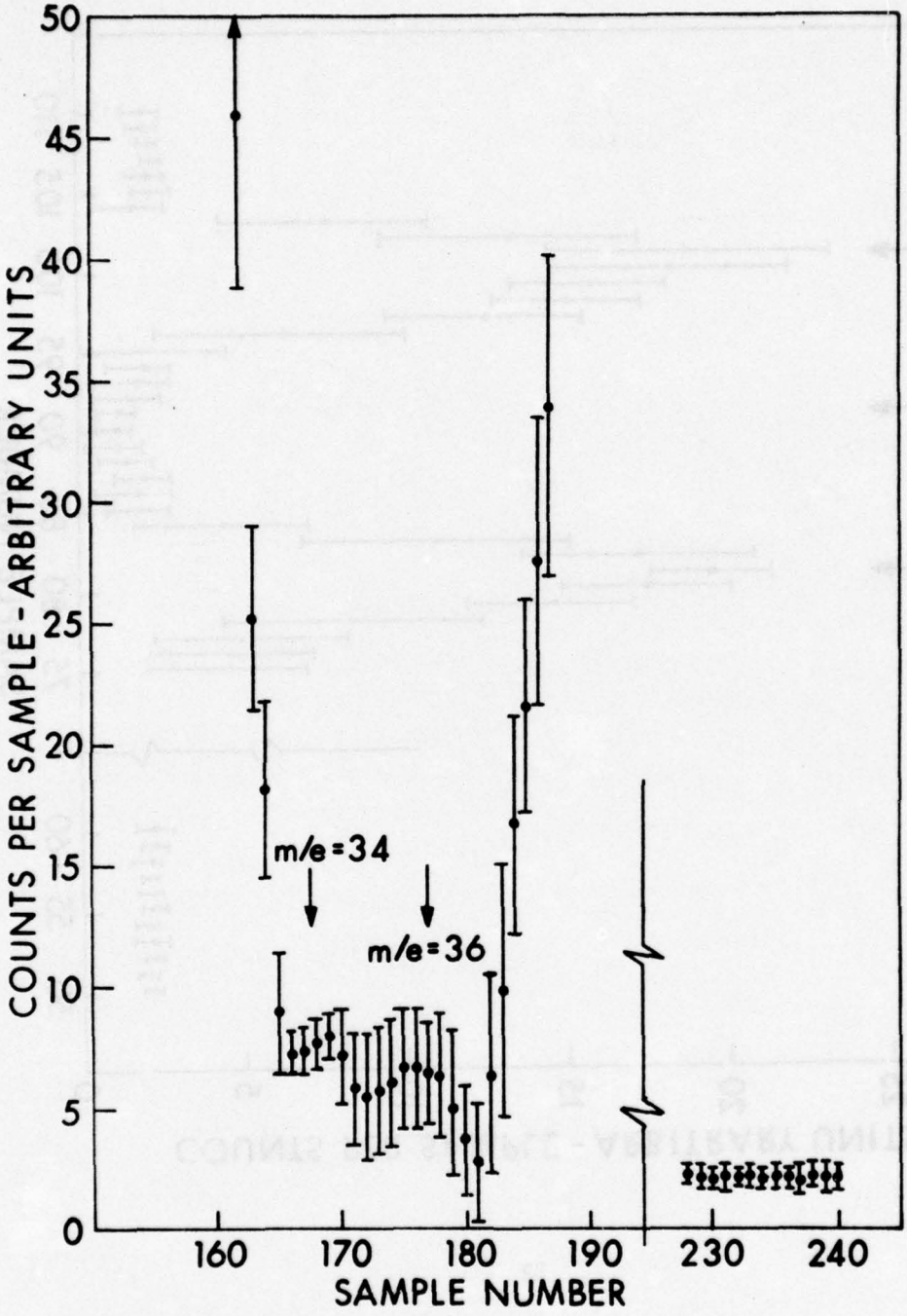

Figure 6. Details of the oxygen-isotope and argon-isotope area of the count mode scans. The round dots denote the mean count rate at each sample point; the error bars show the uncertainty of the determination of each mean.

852 ppmv, and scales the H_2O uncertainty, one finds that 1σ of the count rate at m/e = 18 is about 39 ppmv. If one scales the difference between the m/e = 36 peak height and the background level, divides it by 7 (because an argon peak will be inflated by that amount), assumes it is due to a gas with a volume mixing ratio of 31.5 ppmv, and scales the H_2O uncertainty, one finds 1σ of the count rate at m/e = 18 is about 29 ppmv. The agreement, considering the assumptions, is remarkably good, and we adopt 40 ppmv as the sensitivity of the instrument. This analysis does not include the effects of differences in ionization efficiencies or detection efficiencies (for species other than N_2, O_2, and Ar). The analysis is not valid for argon, neon, helium, and other gases for which the pumping rate difference enters the sensitivity calculation significantly.

One can carry this analysis one step further and ask what the effect on the ion distribution could be expected to be if a sampling package carried aloft enough water to raise its mixing ratio to 40 ppmv. If one assumes that the ions are of the form $H^+(H_2O)_n$, the total gas pressure is 274 Pa (2.05 Torr), the gas temperature is 250 K, and $[H_2O]$ = 4 ppmv,[20] the ions at mass-to-charge ratios of 55, 73, 91, and 109 have percentages of the total amounting to 20.8, 77.9, 1.3, and 0.[13] If $[H_2O]$ = 40 ppmv, the percentages are 2.2, 83.4, 14.3, and 0.1, respectively. Thus the distribution would shift somewhat toward larger masses, but the shift would be much smaller than the one added water molecule. A decrease in temperature of only 17 K, with $[H_2O]$ remaining at 4 ppmv, would shift the ion distribution toward larger masses as much as an increase of $[H_2O]$ to 40 ppmv.

VIII. COMPARISONS, CONCLUSIONS, AND PLANS

A. Comparisons. Figure 7 is a current-mode scan reproduced from the work of Woods.[8] Comparison with Figure 3 shows the progress that we have made in balloon flights of mass spectrometers. The flight which carried Woods' mass spectrometer used a 390 m load line to separate the gondola from the balloon. However, Woods' mass spectrometer and other instruments on the gondola[21,22] agreed that there was a high background

[20] The water vapor volume mixing ratio at 40 km may be as large as 10 ppmv, according to C. P. Chaloner, J. R. Drummond, J. T. Houghton, R. F. Jarnot, and H. K. Roscoe, "Stratospheric measurements of H_2O and the diurnal change of NO and NO_2," Nature 258, 696 (1975).

[21] H. N. Ballard, R. W. Byrnes, M. Izquierdo, J. Whitacre, and C. McDonald, "Determination of Neutral Constituent Concentrations in 45- to 60-kilometer Interval with Rocket- and Balloon-Borne Samplers," Chapter 8 in "Stratospheric Composition Balloon-Borne Experiment - 18 September 1972," compiled by H. N. Ballard and F. P. Hudson, ECOM-5554, Jan 1975, and Trans. Am. Geophys. Soc. 54, 1150 (1973).

[22] P. Goodman, "Water Vapor Measurements during a 48-km Balloon Flight," Chapter 10 in "Stratospheric Composition Balloon-Borne Experiment - 18 September 1972," compiled by H. N. Ballard and F. P. Hudson, ECOM-5554, Jan 1975.

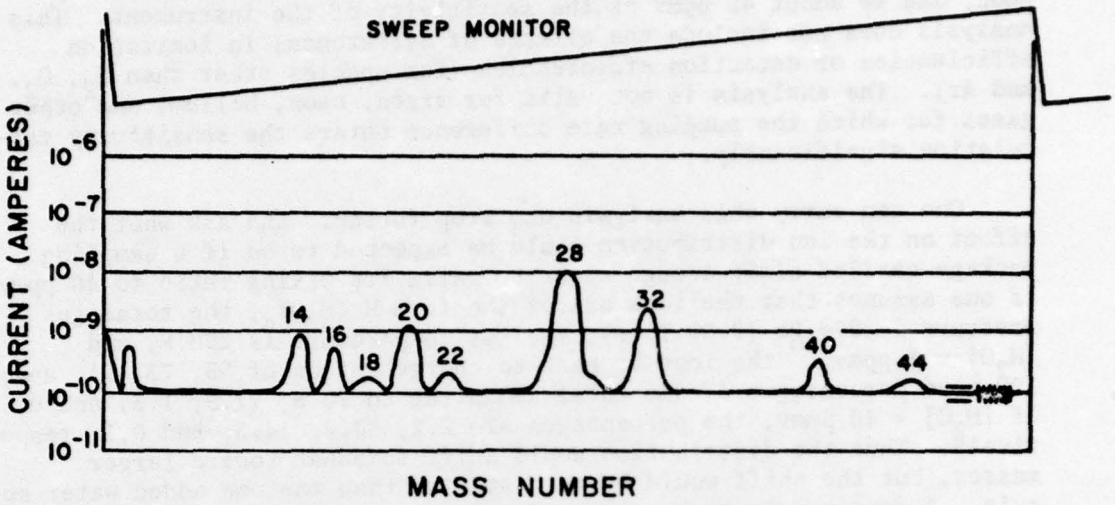

Figure 7. Current-mode mass spectrum reproduced from Reference 8.

water vapor density throughout the flight. They concluded that this background was due to water carried aloft by the balloon and desorbed during ascent and float. Our success suggests another interpretation of their results, that the water they saw came from outgassing of the experiments, control packages and parachute, all of which were close to the mass spectrometer and none of which were designed for clean flight. Their high background could be accounted for by much less water carried aloft on the items surrounding the sampler than the water the balloon would have to have carried.

B. Conclusions. The most important conclusion is that the sampling of ions by this package was not efficient enough to measure ion distributions in the stratosphere. However, the next most important conclusion is that a clean package has been flown in a manner which has been demonstrated to be clean enough for sampling to be meaningful. The basic techniques of the experiment, in terms of on-board and ground data handling and commands, have been shown to be sound.

The cosmic ray ionization chamber may have to be redesigned for meaningful data to be obtained. The temperature sensors must be altered in manner of operation and/or in mounting to obtain good stratospheric temperatures. Telemetry techniques were demonstrated to work, but there must be improvements for full benefits to be reaped from real-time data acquisition and processing.

C. Plans. A second mass spectrometer sampling package is in the final stages of construction at the University of Denver. It incorporates the best of the ideas of the first package, but has a bigger aperture, longer sampling time and much larger pumping capacity. It will be used for studies of stratospheric negative ions and positive ions. The first flight of this instrument is planned for the fall of 1976.

Separate laboratory studies on the sampling of thermal ions have been underway for some time at the University of Denver. The laboratory apparatus features an easily modifiable sampling arrangement. Optimum ion sampling efficiencies for a given pump size and external gas pressure are being sought. The results of these experiments will be incorporated into the sampling package.

IX. ACKNOWLEDGEMENTS

This effort profited greatly from discussions with R. O. Woods at Sandia Laboratories. He and H. N. Ballard at ASL contributed significantly to this work from their experience in ballooning. The efforts of the National Scientific Balloon Facility are gratefully acknowledged. E. P. Weaver at BRL and J. Van Allen at DU are to be congratulated on the construction of the remarkable real-time data analysis program. Those who built the package, only to see it die on a rock in Texas, are

to be commended for their perseverance: J. R. Olson, R. C. Amme, D. G. Murcray, J. N. Brooks, D. A. Steffen, R. E. Sturm, P. R. Williamson, F. E. White, J. J. Kosters, G. L. Mason, and A. DeKlerk. Finally, I thank F. E. Niles for his support during the course of this work.

APPENDIX

A. Introduction. Rocket-borne mass spectrometers for the study of ions in the lower ionosphere have used draw-in potentials on floated aperture plates to encourage ions to enter the spectrometer.[23,24] Up to +40V has been used for negative ions,[24] and -8V has been used for positive ions.[23] It has been suggested that photoemission of electrons from the surface of a sampling package in the stratosphere would cause a balloon-borne package to come to a "slight" net positive potential with respect to the ambient environment,[25] with the result that positive ions would be repelled by the package.

This appendix contains results of considerations of the most appropriate size for the aperture plate and what its potential should be. Since a wind at the package has been suggested as an aid in sampling into a charged package,[25] that too has been included. Finally, the appendix concludes with an argument against appreciable package charging in the stratosphere.

B. The Effect of a Charged Package. The package geometry which has been assumed is shown in Figure 8. Cylindrical geometry has been assumed throughout, even though the sampling face of the package is square. The solution for Laplace's equation, $\nabla^2\phi = 0$, has been sought for a variety of situations. The field due to charged particles in this space has been neglected because of their low number density.

This problem in electrostatics has been solved analytically,[26] but the solution does not permit one to change geometries to aid ion collection. We used an iterative "relaxation technique" to find the potentials $\phi(r,z)$ which satisfy Laplace's equation for the given probe (or aperture plate) size, probe potential, and gondola (or package) potential. The space below the package has been assumed to be cylindrically symmetric. The r-z plane is divided into a grid of 30 x 20 discrete cells, as shown. The r dimension of each cell has been taken as 0.5, the z dimension 1.0 in all cases. All sizes are in relative, "dimensionless" units.

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[23] R. S. Narcisi and A. D. Bailey, "Mass Spectrometric Measurements of Positive Ions at Altitudes from 64 to 112 Kilometers," J. Geophys. Res. 70, 3687 (1965).

[24] R. S. Narcisi, A. D. Bailey, L. Della Lucca, C. Sherman, and D. M. Thomas, "Mass spectrometric measurements of negative ions in the D- and lower E-Regions," J. Atmos. Terr. Phys. 33, 1147 (1971).

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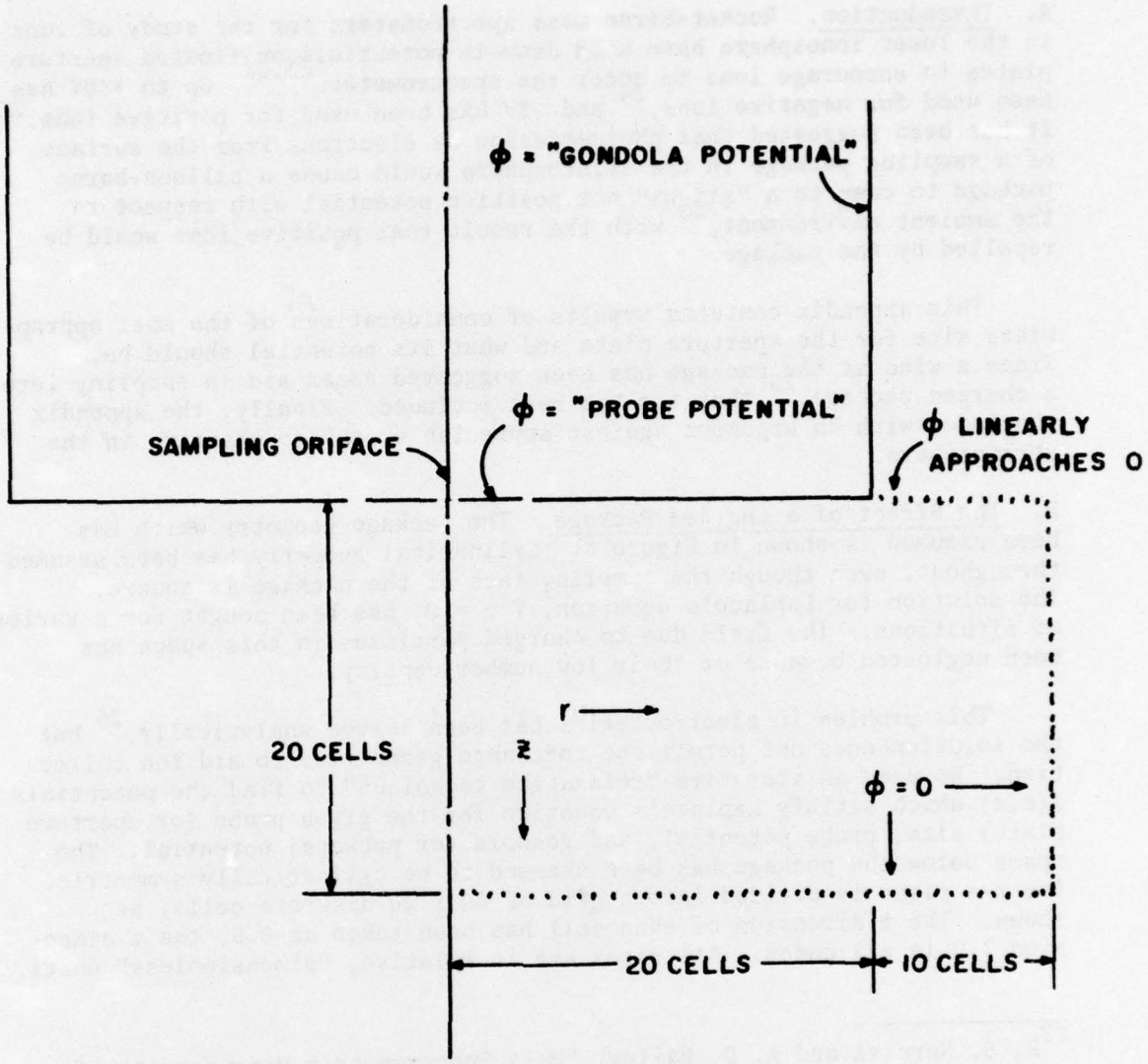

Figure A1. The package geometry assumed for studies of package charging. (z = 1 on the gondola surface and r = 0.5 on the centerline.)

The results of the calculations are listed in Table 1. It is assumed that positive ions could be collected if a positive ion at infinity and ϕ = 0.0V could find a path with monotonically decreasing potentials leading to the aperture plate (or probe).

Table 1 shows that if the probe radius is 3 (and the gondola radius is 20), a -20.0V probe potential permits ions to be sampled even though the gondola potential is +0.5V. If the probe radius is limited to 2, the gondola cannot be more positive than 0.2V, and if the probe radius is only 1, ion collection will take place only for gondola potentials less than 0.065V or 65mV.

TABLE A1. ION COLLECTION WITHOUT WIND

Probe Radius (in cells)	Probe Potential (Volts)	Gondola Potential (Volts)	Collection Successful?
2	-15.0	0.5	No
3	-15.0	0.5	No
3	-20.0	0.5	Yes
2	-20.0	0.4	No
2	-20.0	0.3	No
2	-20.0	0.2	Yes
1	-20.0	0.2	No
1	-20.0	0.1	No
1	-20.0	0.07	No
1	-20.0	0.065	Yes

The effect that a relative wind on the package might have on these calculations was considered next. Williamson suggests that a horizontal (r direction) wind would overcome many of the problems caused by a positive package potential.[25] Inclusion of the wind necessitated the addition of a transport calculation to the electrostatic results. The following assumptions were made: ion mobility, 2.0 x 10^{-4} m^2/V sec (2.0 cm^2/V sec); gas temperature, 250 K; gas pressure, 274 Pa (2.05 Torr); wind speed, 0.57 m/sec; wind in the r direction only, no z component. The calculation includes the effects of diffusion of the ions to the gondola surface where they are neutralized. The FORTRAN program that was used for these calculations permits one to start an ion at any value of z greater than 1 and follow the ion's drift in r - z space. Collection is assumed to have taken place if ions can reach the center of the aperture plate before being blown past it by the wind.

These calculations show that if there is a wind, ions are successfully collected with a somewhat smaller probe voltage, all other conditions remaining the same. The ions that are collected are ones that have been blown across the bottom of the gondola by the wind, which overcomes the slightly repulsive potential and permits the ions to get into the attractive field of the aperture plate. Ion diffusion to the bottom of the gondola depletes these ions a negligible amount.

Finally, a 2 m by 2.7 m stainless steel screen was suspended below the aperture to help create a field-free region for the ions, strengthen the shock-absorbing leg arrangement, and help protect the bottom of the gondola from damage on impact. When the effect of the screen is added to the calculations, one finds that it aids ion collection somewhat, that is, permits ion sampling from a somewhat larger volume if there is a wind. If there is no wind at all (a very unlikely event), the screen makes very little difference in the sampled volume.

C. An Argument Against Appreciable Package Charging. Suppose that low-energy electrons were photoelectrically emitted from the package surface by the ultraviolet component of the sun's rays. For a package to acquire a significant positive potential would require that the electrons continue to travel away from the package far enough to escape its influence.

The distance that an unattached electron could travel away from the package can be estimated from available data. The pressure at 40 km altitude is about 274 Pa (2.05 Torr) so that the mean free path between electron-molecule collisions is less than 1/4 nm.[27] An idea of the angular distribution of these scattered low energy electrons can be obtained from Massey, *et al.*[28] For 3.7×10^{-19} J (2.3 eV) electrons, one can expect half the collisions to change the electrons' direction of travel by more than 90°; that is, to backscatter the electrons. For 6.4×10^{-19} J (4.0 eV) electrons, the fraction backscattered per collision is smaller, but sizable. One can infer from this that low energy electrons escaping from the package surface while floating in the stratosphere would have their directions randomized within several collisions, that is within a fraction of a millimeter from the package surface. Further, low-energy electrons could be expected to attach to oxygen molecules to form much less mobile negative ions. Both the electrons and negative ions would be attracted back to the package if its potential became slightly positive with respect to that of the undisturbed stratosphere. At worst, a layer of negatively charged particles might build up a fraction of a millimeter away from the positively charged package. To an ion more than a few millimeters away, however, the net package potential would appear to be the ambient stratospheric potential. Thus, the effect of photoelectric emission of electrons from the package surface should not interfere with sampling into packages through an attractive aperture plate of a few millimeters diameter.

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