Instruments and Techniques
for Stratospheric Research

The Cover

An enlarged view of the central chamber in an instrument that detects stratospheric trace elements by resonance fluorescence, depicted here against a background of chemical symbols for substances measured by the techniques described in this issue. See Fig. 15 on page 63 for a more complete view; the article that describes this instrument begins on page 55.

INSTRUMENTS AND TECHNIQUES FOR STRATOSPHERIC RESEARCH

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INSTRUMENTS AND TECHNIQUES FOR STRATOSPHERIC RESEARCH

Contents

In-Situ Mass Spectrometry at Stratospheric Altitudes

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Balloon-borne experiments aimed at measuring atmospheric composition can be divided into two general categories. In one, the mean properties of a column of air more or less remote from the instrument are investigated by techniques such as optical spectroscopy. In the second, the properties of a sample taken in the immediate vicinity of the payload are investigated. This may be done either by on-board analytic instruments or by techniques by which the sample is stored to be analyzed later in the laboratory.

We will discuss here the application of one technique for in-flight analysis. This technique, or indeed any technique which is to be used in the flight environment, will never compete in sensitivity or range with analysis performed in the laboratory. Flight techniques do, however, possess advantages which make them attractive for certain studies. For example, it is possible to obtain continuous—or nearly continuous—data during time intervals of particular interest, such as sunrise or sunset. In-flight analysis is almost mandatory for chemical release experiments, in which a puff of gas is released and the time history of its interaction with the ambient atmosphere is studied. Here the need is for data that are continuous in time and are taken at a known point in space. And if properly performed, an in-situ analysis is not subject to artifacts caused by prolonged contact with the walls of a container where outgassed products might be introduced into the sample and where recombination and chemical reactions take place to an indeterminate degree.

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Relative Merits of the Technique

Mass spectrometry, the subject of this article, has a number of distinct advantages for atmospheric research. The ones best exploited are its ability to give continuous data regarding concentrations of any species which it can sense, its ability to identify a wide variety of species not necessarily specified a priori, and its ability to detect ionic as well as (or better than) neutral constituents. Its greatest disadvantages are its inability to detect neutral trace constituents below the parts-per-million level for most species and occasional ambiguities caused by species having similar mass numbers.

There are a number of general types of mass spectrometers, but all have certain operational features in common. In every case, the species of interest is transformed into the gas phase (unnecessary in the case of atmospheric research where the subject is already a gas), ionized (usually by bombardment with a beam of electrons), and caused to move (usually by an accelerating voltage). When the ions are in motion, their electrical charge provides a "handle" by which they can be manipulated with a controlled electrical or magnetic field. Such a field exerts a force upon an ion that is proportional to its electrical charge. This force divided by the mass of the ion is a measure of the acceleration imparted by the field to the ion. Thus a mixed beam of ions can be resolved into a number of discrete "rays," each having a given mass-to-charge ratio (M/e). These can be detected at different points within the "analyzer" portion of the instrument or, alternatively, caused to pass one after another through the same point by varying the intensity of the field. Ions are most easily detected by an electric current sensor (electrometer), usually with an electron multiplier as a first-stage amplifier. The electrical current at a given value of M/e is an indicator of the relative abundance of an ionic species. Thus, as the instrument is scanned over some range of M/e, the output takes the form of a series of peaks of varying amplitude. This is the mass spectrum of the mixture.

It is possible to detect very small concentrations of ambient ions because the mass spectrometer ignores neutrals when configured to detect ions. Unfortunately the reverse is not true; when a mass spectrometer is looking at neutrals, the ions are lost in the background. In the case of our instrument, we have demonstrated a sensitivity adequate to detect normally occurring densities of nitric oxide ions (NO^+) at altitudes in the vicinity of 50 km, although the data were statistical in nature and not adequate to establish absolute concentration levels. This points out another difficulty involved in the application of mass spectrometry—the fact that, although it is easy to

obtain data regarding relative concentrations and changes, it is difficult to measure absolute concentrations. The greatest value of flight mass spectrometry is thus in perturbation studies, where the response of the atmosphere to inputs such as diurnal variation of solar radiation or artificial chemical releases is reflected in concentration changes. Also, since the instrument need not be specifically set up to look at a chosen species, a single experiment might involve measuring concentrations of a range of constituents such as nitrogen oxides, hydrated ions, and chlorine compounds——all preferably in the ionic state.

System Description

The flight system described here grew out of an instrument originally developed for application on sounding rockets. Because of the environment for which it was designed, the analyzer itself was immediately adaptable to balloon experiments, being rugged and lightweight. It was necessary, however, to add a pumping system in order to allow the instrument to operate at the lower altitudes and higher densities of a balloon experiment. This had not been necessary in previous experiments at rocket sounding altitudes.

The mass analyzer is a radio frequency (RF) quadrupole of the type described in the landmark paper of Paul, Reinhard, and von Zahn (1958). The rods are arranged around an inside radius (r_0 in the usual notation) of 2.5 mm. Their length is 12 cm. The instrument operates at a frequency of approximately 1 MHz.
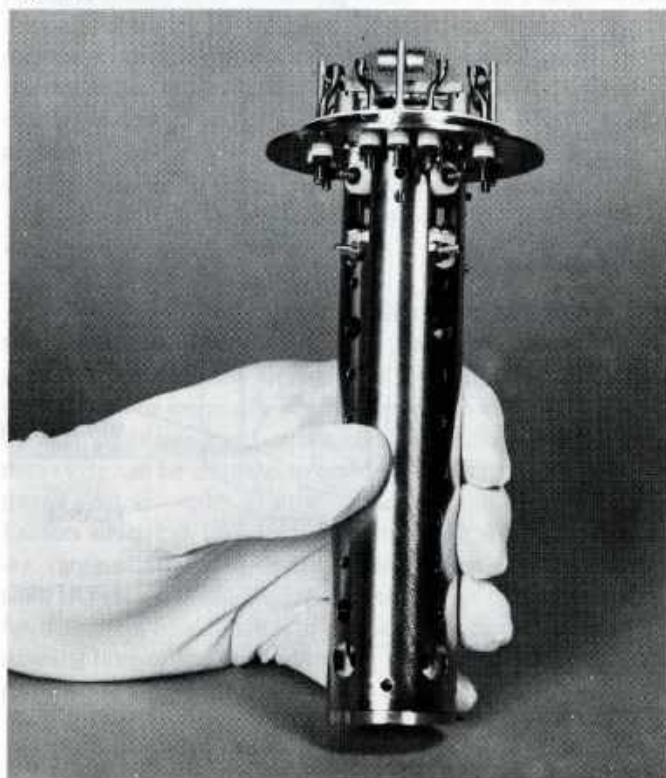
In a quadrupole mass spectrometer, a beam of ions that is to be resolved into bundles of ions having discrete values of M/e is injected into the electrical field produced by four parallel electrodes. A bias voltage is superimposed upon a radio frequency voltage to produce an electrical field that has the property of allowing ions of a value of only 1 M/e to traverse the analyzer at a time. As the voltages are swept, successive ionic species appear at the outlet of the analyzer and are detected by an electron multiplier. The mechanism by which this separation takes place is described in easily understood terms by Dawson and Whetten (1968).

In the original (rocket) configuration, shown as Fig. 1, the analyzer was equipped with a seminude ion source in the interest of minimizing the recombination of atomic oxygen on surfaces——a problem later solved by the introduction of an enclosed, cryogenically cooled ion source (Offermann and Trinks, 1971). In Fig. 1, the analyzer is shown with the ion source at the top, as it would be in a rocket experiment. The quadrupole rods are located inside a perforated cylindrical housing and are not visible in the photograph. When adapted for balloon use, the analyzer was mounted in an inverted position, the inlet to the system being at the bottom.

In order to adapt it for balloon experiments, the analyzer was fitted with a sample induction system, which incorporated a valve and an enclosed ion source that had the unusual characteristic of allowing the unobstructed passage of ambient ions into the inlet aperture, through the source, and into the analyzer. The arrangement is diagrammed in Fig. 2. A sample of the ambient atmosphere is admitted when the valve is opened upon command from the ground. The gold-plated Teflon plunger was originally actuated by a rotary solenoid/cam mechanism. This was replaced on subsequent flights by a pneumatic bellows assembly.

Conflicting pressure requirements had to be satisfied by the pumping arrangement. It was desirable that the pressure in the analyzer and in the electron multiplier, which is located at its far end, be kept as low as possible. This was done to prevent scattering of ions by background molecules within the analyzer and to prevent arcing of the high-voltage electrodes of the Johnson Laboratories type MM-1 multiplier. On the other hand, it was desirable that a higher pressure (10^{-4} torr, or 1.3×10^{-2} N/m^2) be maintained in the ion source in order to produce a large number of ions when the instrument was operated in the neutral mode. Differential pumping was accomplished by allowing the ion source to communicate with the body of the pump through a replaceable aperture. This made it possible to trade off the sizes of the inlet "pinhole" and the exhaust aperture to control the pressure in the source
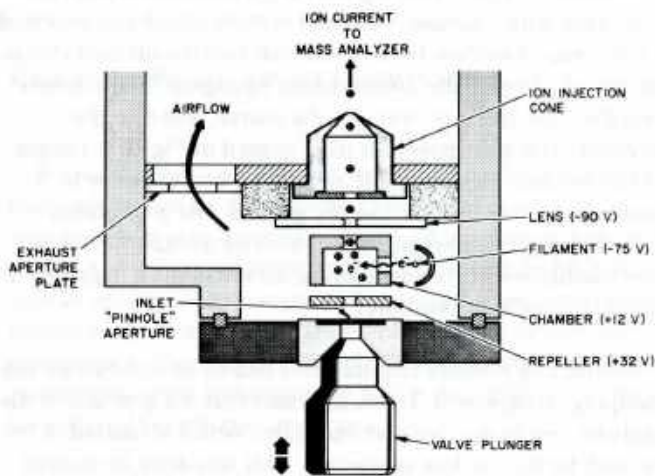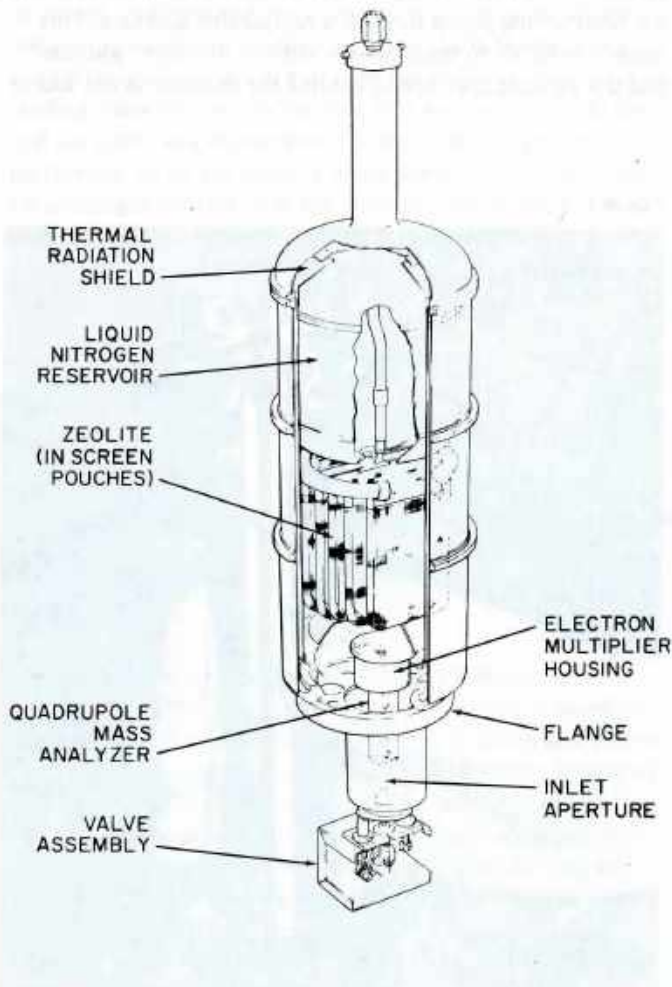
Figure 1.

Figure 2.

Labels in Figure 2:
ION CURRENT TO MASS ANALYZER
AIRFLOW
ION INJECTION CONE
EXHAUST APERTURE PLATE
LENS (-90 V)
FILAMENT (-75 V)
INLET "PINHOLE" APERTURE
CHAMBER (+12 V)
REPELLER (+32 V)
VALVE PLUNGER

Figure 3.

Labels in Figure 3:
THERMAL RADIATION SHIELD
LIQUID NITROGEN RESERVOIR
ZEOLITE (IN SCREEN POUCHES)
ELECTRON MULTIPLIER HOUSING
QUADRUPOLE MASS ANALYZER
FLANGE
INLET APERTURE
VALVE ASSEMBLY

chamber. The pressure in the pump itself was typically in the 10^{-7}-10^{-8} torr ($\sim$1.3 X 10^{-6} N/m^2) range.

This system was developed for use in the "Stratcom" series of balloon experiments, in which a large number of experiments have been flown in single payloads to obtain simultaneous measurements of related parameters. Since it was not intended that an entire payload be committed to the mass spectrometer, and since the total scientific payload of the first flight was to have a mass of no more than 113 kg, a system was required which was light in weight and which consumed a minimum of power. Sampling was to be performed intermittently over a period on the order of one day. This meant that the system required a high pumping speed combined with economical use of commodities such as cryogens or battery power during the "standby" periods.

Cryopumping

After an extensive investigation into the power requirements and concomitant battery weights of active pumping systems, it was decided to use a non-power-consuming cryopump (Stern and DiPaolo, 1969). With this system a quantity of zeolite (Linde 5A) is chilled by liquid nitrogen and serves to adsorb the gas within the vacuum system. This has the advantage of requiring no on-board power source; the only thing being consumed is the cryogen needed to maintain the necessary low temperature against heat absorbed during the flight. A high intermittent pumping speed, combined with the ability to recuperate between samples, is obtained by packaging the zeolite in a geometry with a high surface-to-volume ratio. Cryopumping, which is essentially a surface effect, takes place at a high rate on the surface of the package during sampling. During the standby periods, the adsorbed gas redistributes itself by diffusing to the interior of the package, thereby reestablishing the surface capability for high momentary pumping speed.

The primary disadvantage of zeolite pumping at liquid nitrogen temperatures lies in its inability to pump certain gases, such as helium and neon. As a result, a sizable background of these gases builds up within a pump. If necessary, these gases can be removed by adding a small-capacity appendix pump to the system and expending the power necessary to operate it. In our case the background of noble gases has never become high enough to warrant supplementary pumping.

A cutaway drawing of the flight pump is shown in Fig. 3. It can be seen that the geometry closely resembles that of a conventional Dewar. The cryogen is contained by an inner vessel which is insulated by vacuum and by radiation shields. This is in direct contrast to most laboratory cryopumps, in which a zeolite container is immersed in a cryogenic bath and

heat is abstracted from the outside of the package. Here the zeolite, in pellet form, is contained in a number of screen pouches, which serve to provide the favorable surface-to-volume ratio. Liquid nitrogen circulates from the reservoir through a manifold into U-tubes which are in contact with the zeolite. Heat conduction is promoted by copper sheets which fill the areas bounded by the tubes.

It is necessary to outgas zeolite by baking it under vacuum before use. This is accomplished by circulating heated air from an external oven through the central vent tube in the cryogen reservoir and into the U-tubes. Pumping is done by a mechanical forepump, which is mated with the system by means of a copper tube (not shown) that is pinched off before flight.

The quadrupole analyzer is mounted below the zeolite package, with its inlet at the very bottom of the vacuum system. Below this, outside the vacuum shell, is the valve assembly. Figure 3 shows the older, solenoid-operated mechanism. This proved to be too shock-sensitive for reliable operation during launch and was replaced with a very positive-acting pneumatic valve (shown in Fig. 5). At the top of the analyzer is a shielded container for the electron multiplier, which serves to detect and amplify the ion current. Immediately below the multiplier is a pair of modified commercial flanges with copper O-ring seals. When these are disassembled, the system is broken into two entirely divorced assemblies. The upper comprises the cryopump, and the lower carries the mass spectrometer.

Electronics Package

A number of electrical feed-throughs are located in the lower flange. On the inside, connections are hard-wired to the mass spectrometer. Cable connectors on the outside serve to carry bias voltages, filament power, and signals from or to an electronics package. The remote location of this package is dictated by the need to maintain thermal control of the electronics by enclosing all circuitry in a common container and thus having to stabilize the temperature of only a single package. A number of problems follow from this arrangement, among them the tendency of the elastomer cable surfaces to produce spurious gases in the vicinity of the mass spectrometer inlet, the notorious unreliability of cable terminals at the temperatures and pressures common to balloon experiments, and the fact that at radio frequencies more power is dissipated in the cables than in the instrument itself. It is hoped that in future experiments it will be possible to mount the quadrupole electronics in a hermetically sealed package mounted directly on the vacuum system. This will entail either very accurate temperature compensation of the circuitry or thermal control of the mass spectrometer package independent of the main package.

Sample Induction

Since the primary object of the experiment is to sample ambient ions, the immediate vicinity of the mass spectrometer inlet is kept as unobstructed as possible. No draw-in potential is used. Entrainment in the neutral gas flow is relied upon as a mechanism for inducing ions into the instrument. Although inefficient, this method has proven successful in investigating a relatively abundant ionic species (NO^+).

In the case of neutrals, reliance is placed upon the fact that the aperture allows an uncontaminated sample to enter the instrument, at least during portions of the flight in which there is a relative wind from the lower hemisphere viewed by the payload. By using an arrangement which is free of pipes or ducts, we hope to avoid the contamination problems associated with induction of a sample through a channel. As a concurrent effort, we have developed and test flown an ion anemometer which measures relative winds at the payload. This information can be used to support an in-situ experiment by determining those portions of the flight during which the instrument sampled the unperturbed ambient atmosphere. Without relative wind data it is difficult to separate true conditions from perturbations introduced by payload outgassing.

Circuitry

The circuitry flown on the first two experiments to generate time-varying bias voltages and to telemeter signal output operated primarily in the analog mode; the only exception was the pulse-counting circuits used for detection when the instrument was operating in the ions mode. This has been changed in the interest of more readily interfacing with the digital command and control equipment now in use and also to facilitate computerized data reduction. The sawtooth modulation of voltage required to scan a quadrupole mass spectrometer is now generated digitally rather than by a resistance-capacitance network with appropriate amplifiers.

All functions are commanded from the ground, with real-time readouts being provided in the command station. This provides a very flexible arrangement in which unexpected features can be examined in great detail, the mode of operation can be adapted to events such as sunrise or sunset, and the data cycle can be adjusted to factors which cannot be predicted a priori——such as a pressure rise within the pump. Factors which can be manipulated in almost any permutation are: range of mass scan, "peak picking" of any selected mass peak or portion of the range, electrometer or pulse counting for detection, investigation of ambient ions or neutrals, and opening time of the sampling valve. Data are telemetered and recorded at a ground station rather than on board.
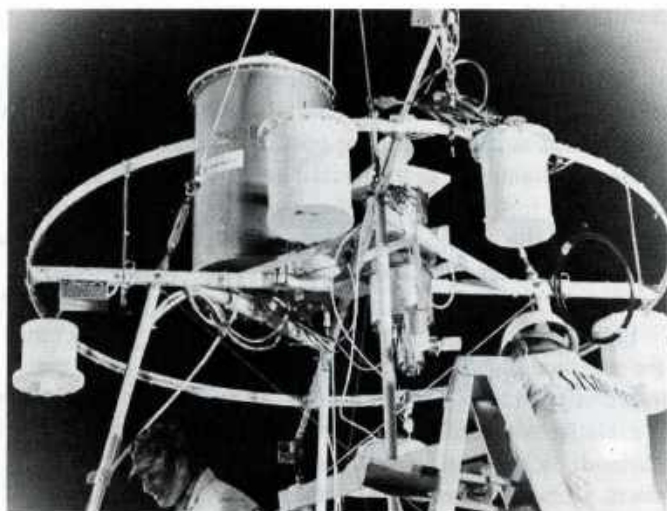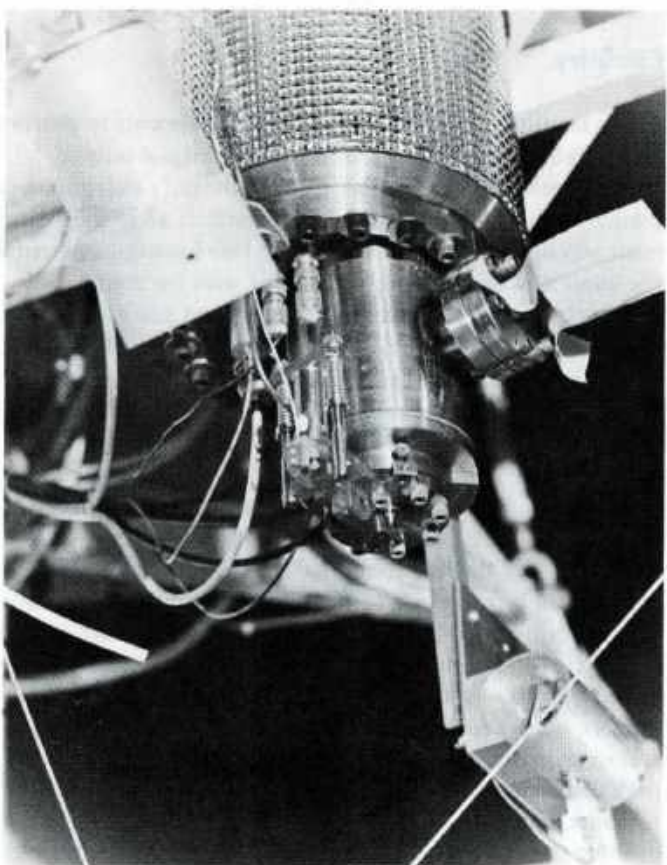
In the process of upgrading the instrument by interfacing it with the digital circuitry, further increase in capability has been made by extending the mass range. The original circuitry was designed to scan only to M/e 50, this being adequate for the limited purposes of the original rocket-borne experiment. For this mass range, the peak amplitude of the radio-frequency voltage applied to the analyzer was only 25 V, a value fairly easy to reach with low-power, solid-state circuitry. Since the greatest interest is now in hydrated ions and other heavier species, the mass range has been extended to approximately 150. This requires a peak RF amplitude on the order of 70 V. Generating such voltages within the close tolerances required by the instrument using miniaturized circuitry is not a trivial problem——particularly when transmission lines on the order of a meter in length are involved.

Flight Experience

Figure 4 shows the mass spectrometer installed in the airframe before its second flight (from the NCAR facility at Palestine, Texas). The surface of the cryopump has been shrouded with a Mylar "space blanket" for additional thermal insulation. This photograph was taken during an early stage of final flight assembly; for this reason a number of pieces of ground support paraphernalia are in evidence. A large square of foam, for example, can be seen in place around the neck of the Dewar. This was intended to prevent condensed water from running down the outside of the cryopump. It was removed before flight.

Figure 5 is a close-up of the second version of the inlet valve, taken at approximately the same camera angle. Another block of Styrofoam can be seen taped to the small flange on the right of the assembly. This served to protect the copper tube pinch-off during payload assembly. The Teflon valve plunger can be seen at the center of the bottom flange. To the left of it is a pair of springs which exert force upon a lever to close the valve. Between the springs is a small cylinder containing a pneumatically operated bellows which is pressurized to open it.

The white object in the foreground and the open-ended horizontal cylinder at the rear composed a cooperative experiment fielded by L. Hale of Pennsylvania State University. The horizontal cylinder contained a Lyman-alpha lamp which could be turned on to irradiate the vicinity of the mass spectrometer inlet. When this was done, NO^+ ions were produced in the ambient air and then detected by the mass spectrometer. The white object is an ion probe, used primarily for diagnostic purposes in this experiment. The Lyman-alpha experiment was partially successful in that the mass spectrometer showed itself capable of detecting NO^+ ions in the concentrations actually present. The data were, however, otherwise anomalous, apparently due to photoemission of electrons from metal

Figure 4.

Figure 5.

surfaces under bombardment by the ultraviolet radiation. The only surprise provided by the second flight data was the indication of extremely high background levels of water vapor, caused by outgassing of the payload.

Figure 6 shows a preflight sample spectrum. This covers the mass range up to approximately 50 atomic mass units (AMU). The output is logarithmic, adjusted to one decade per graticule unit. The blunt shapes of the peaks are due to the logarithmic compression. Note that there is a dynamic range of 10^3 between the lowest and highest peaks. The data channel extended for another decade above the highest peak. The flat base line was due to the fact that the electrometer had a finite threshold, below which it transmitted zero signal.

The pump shown in Fig. 4 is the same unit that had been flown in the first experiment. It showed remarkable shock resistance. It has now survived two parachute landing impacts and still retains its vacuum integrity. It has been retired, but is being used as a backup unit. Reconditioning it for flight proved to be easier than anticipated.
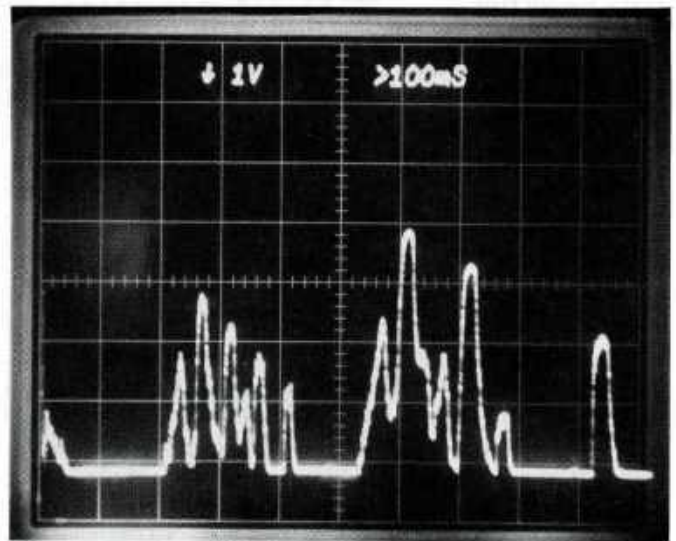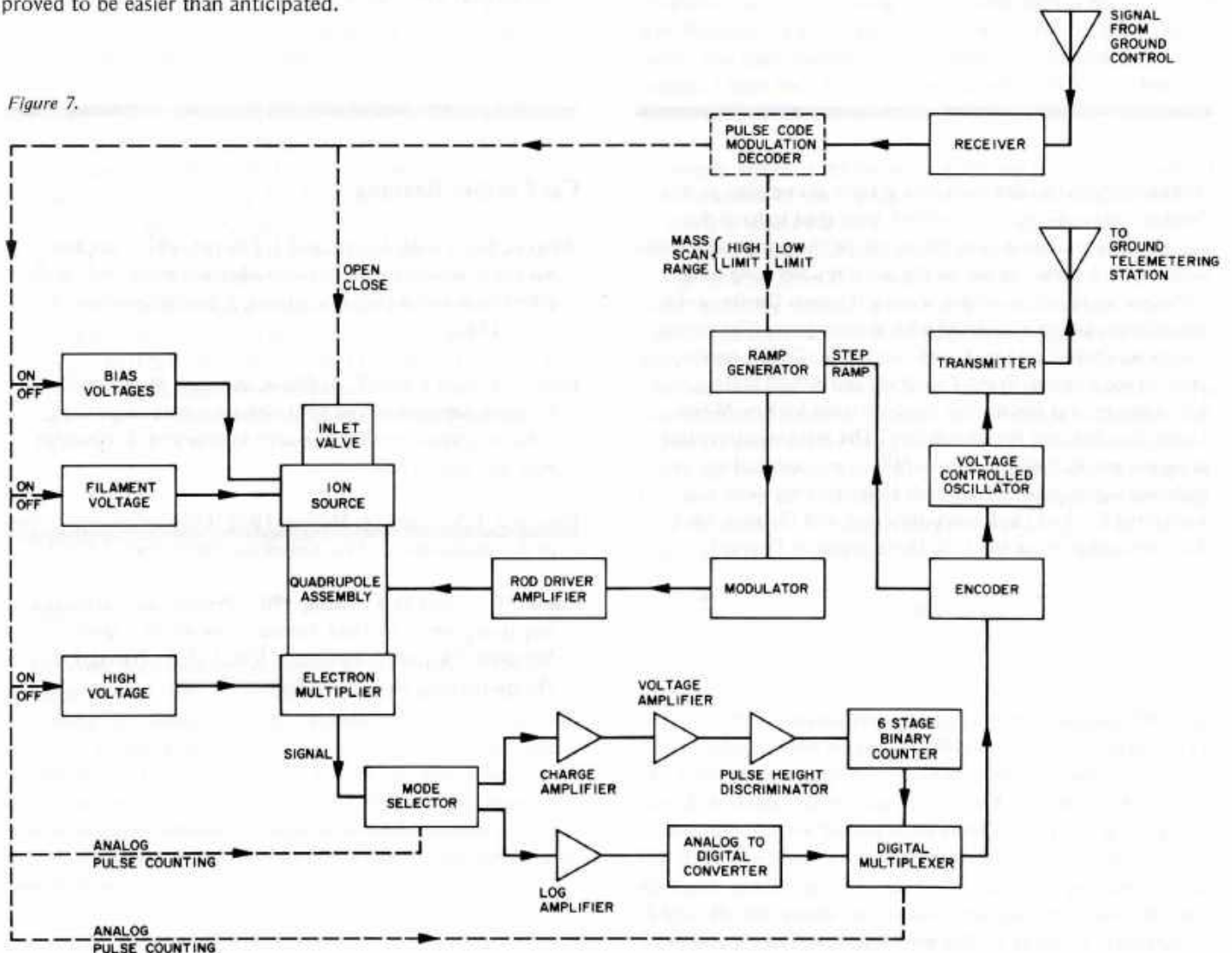

Figure 6.

Figure 7.

Data Reduction

On earlier flights, data were either telemetered in the analog (logarithmic electrometer) mode or as a series of ion counts every 0.01 s. In either case, data reduction was a slow process because each point had to be dealt with manually. Computer interfacing for data reduction has been facilitated by putting the output into a computer-compatible format. Output from either the electrometer or the pulse-counting mode is transmitted in digital form, along with the corresponding value of the ramp voltage at the time the datum was taken. The system which accomplishes this is shown in Fig. 7, along with the elements which control the mass scan and other functions. Data are transmitted at a rate of 37.5 frames per second; each frame contains the value of the ramp voltage at that time and three successive values of (digitized) signal current or count rate. The ramp, which is generated digitally, advances the RF voltage in increments of four steps per AMU. The increments are smoothed in the output circuitry so as to give a continuous scan rather than a stairstep.

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