5. MEASUREMENT AND IDENTIFICATION OF STRATOSPHERIC IONS

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ABSTRACT

Recent progress in the technology of stratospheric ion mass spectrometry is described.

The state of the art as well as some typical measuring problems and needs for future developments are briefly reviewed.

INTRODUCTION

Penetration into the atmosphere of high energy particles and short wave radiation such as solar UV light, X rays and cosmic rays, results in formation of charged particles through direct ionization processes. At sufficiently high gas densities, ions and electrons thus formed make multiple collisions with neutral particles, and electron attachments as well as ion-molecule reactions occur, modifying the identity of the charged particles. In the stratosphere the main ionization source is cosmic radiation and the lifetime of ions is of the order of 100 to 3000 s between 15 and 40 km. The subsequent rapid ion-molecule reactions involve different trace gases so that the terminal ions have a totally different nature than the primary ones.

Until 1977, the experimental data on stratospheric ions were limited to total ion density and mobility measurements (PALTRIDGE, 1965; BRAGIN et al., 1966; ROSE et al., 1972; WIDDEL et al., 1977; BRAGIN, 1967; MORITA et al., 1971; MITCHELL et al., 1977).

Information on positive and negative ion composition below 50 km was based on modelling (FEHSENFELD and FERGUSON, 1969; MOHNEN, 1971; FERGUSON, 1974; REID, 1979), and extending the framework formerly developed for D-region ion chemistry. Therefore it remained merely speculative and incomplete. Nevertheless, such information is important for several reasons:

- Knowledge of the nature of stratospheric ions is essential for our under-standing of physical processes in the field of atmospheric electricity. The conductivity of the atmosphere, for instance, depends upon ion mobility and thus on ion composition.
- Also, stratospheric ion mass spectrometry may become an important tool for detection of trace gases with very low concentrations (ARNOLD et al., 1980; ARIJS et al., 1983a,b; VIGGIANO and ARNOLD, 1983).
- Furthermore, stratospheric ions may play an important role in gas to particle conversion and nucleation of stratospheric aersols (MOHNEN and KIANG, 1976; ARNOLD, 1980, 1982), which in turn could influence the Earth's radiation budget and climate.
- Finally, in situ mass spectrometric investigations of stratospheric ion composition can provide experimental thermochemical and kinetic data on ion-molecule reactions taking place under conditions difficult to simulate in the laboratory.

Determination of the nature and abundances of stratospheric ions is there-fore a desirable objective and balloon-borne ion mass spectrometers have been and are developed at several places (ARIJS et al., 1978; ARNOLD et al., 1978; OLSON et al., 1978; CUNNINGHAM and HOFMAN, 1982; BALLENTHIN et al., 1983).

The purpose of this paper is to describe the experimental and technological aspects of such ion mass spectrometers as far as they were available in literature. The scientific results obtained with these instruments have been reviewed elsewhere (ARNOLD, 1980; ARIJS, 1983).

EXPERIMENTAL PROBLEMS AND PAYLOAD DESCRIPTION

In situ stratospheric ion identification requires the development of an instrument, wherein ions are sampled through a small orifice, focussed into an appropriate mass spectrometer and detected after filtering according to their mass to charge ratio. This instrument has an associated electronic package taking care of driving the mass filter and focussing device, delivering high voltage to the detector, recording signals and interfacing between the instrument and the ground-borne experimenter.

For ion composition measurements in the D-region, rocket-borne mass spectrometers have been developed by several groups (NARCISI and BAILEY, 1965; GOLDBERG and BLUMLE, 1970; KRANKOWSKY et al., 1972; ZBINDEN et al., 1975).

Use of similar instruments for stratospheric purposes (ARNOLD et al., 1977) however, poses some severe problems among which short measuring times and ion breakup due to induced shock waves are the most important. For stratospheric measurements it is better to make use of more convenient platforms, such as high altitude balloons which are able to lift heavy and large instruments up to 45 km altitude. Present techniques even allow continuous measurements in an altitude range from 45 down to about 15 km by using valve controlled balloons.

Although the philosophy in designing a balloon-borne mass spectrometer for in situ sampling of stratospheric ions is similar to the one followed in constructing a rocket-borne payload, some important differences evolve from the nature of the problem itself and from the use of a different platform.

A major difference, for example, is the pumping system required to maintain the mass filter in vacuum. Due to the high ambient pressure and the long duration of a balloon flight, a pumping system with a long standing time (several hours), a large pumping capacity and a high pumping speed will be required for a balloon-borne instrument.

A general view of a typical experimental configuration is shown in Figure 1. The gondola consists of three different parts: a cryopump with the mass spectrometer, an electronics compartment and a mechanical support structure. In the configuration of Figure 1, the electronics compartment consists of a light-weight aluminium cylinder, sealed by a large aluminium flange, on which the cryopump is fixed.

This vessel is pressurized with dry air to avoid high voltage breakdown, and contains several electronic modules mounted on platforms parallel to the sealing flange. Hermetically sealed connectors are also provided on the latter for interfacing to telemetry, to telecommand and to devices located outside and for testing the payload. All sealings are realized with special silicone O-rings qualified for a −55 to +200°C temperature range. The mechanical support structure and crash pad are made completely of metal (aluminium) to avoid charging up problems. Its geometry is adaptable to specific needs, such as flying multiple experiment payloads.

In constructing the payload, the use of heavily degassing materials is avoided as much as possible, in view of contamination problems discussed further on.
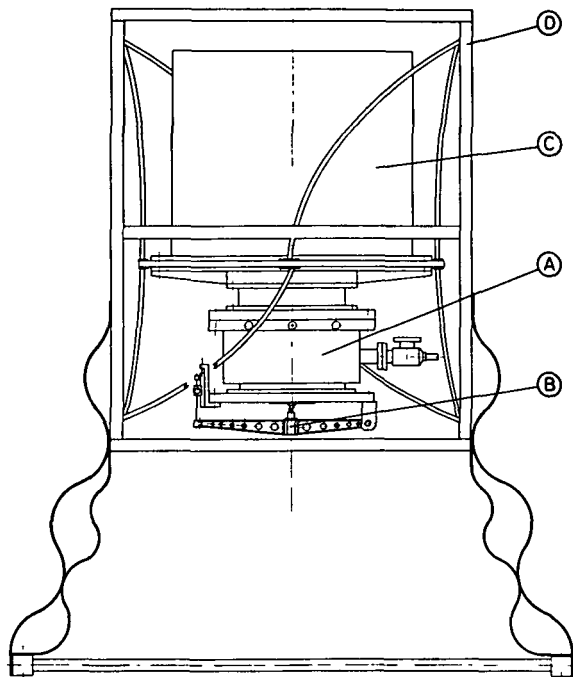
Figure 1. General view of ion mass spectrometer gondola.
A. cryopump; B. opening device; C. electronics container;
D. mechanical support structure.

DETAILED INSTRUMENT DESCRIPTION

(a) High Vacuum Part

The high vacuum part of a typical payload as developed at our institute is pictured in Figure 2. It consists of a high speed cryopump, a sampling hole, a remote opening device and a quadrupole mass filter with an ion focussing device and an ion detector.

In order to prevent scattering of sampled ions by background molecules, to insure proper functioning of the quadrupole mass filter and to avoid H.V. breakdown in the ion detector, a pressure of 10^{-4} Torr or less is required inside the mass spectrometer housing. Since the outside pressure ranges from 1 to 100 mbar, a basic problem of the experiment was designing a balloon-borne pump with high pumping speed. To overcome this difficulty, a liquid helium cryopump was developed, described in detail elsewhere (INGELS et al., 1978) and, therefore, explained here only briefly.

The pump body of the liquid helium cooled cryopump is made of stainless steel and all flanges are sealed with copper or polyimide O-rings. Apart from a glass fibre superinsulation, thermal insulation is achieved through two copper radiation shields, cooled by cold evaporating helium gas passing through an attached spiral. An inner blackened chevron baffle reduces radiation from the ion focussing lens, quadrupole mass filter and ion detector.
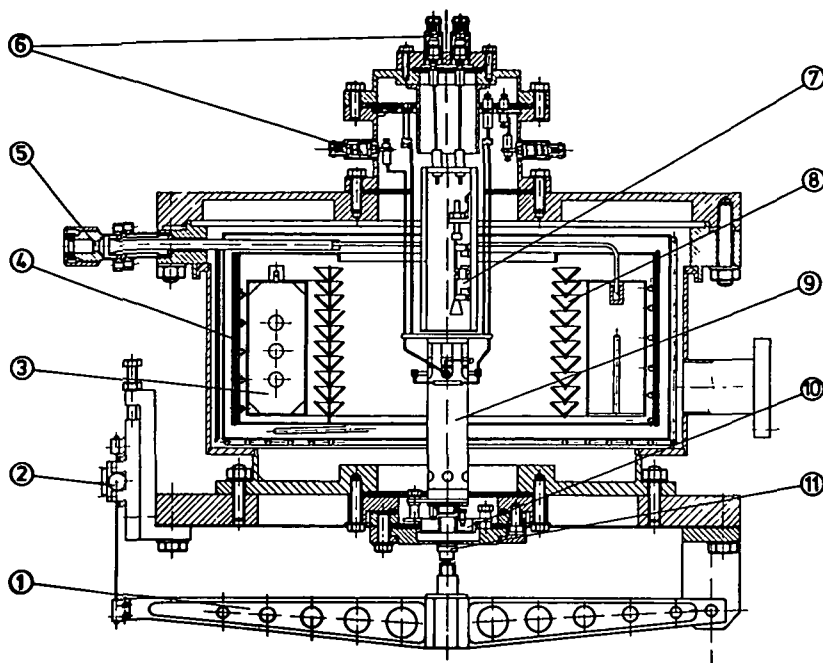
Figure 2. Detailed view of high vacuum part of the mass spectrometer.
1. spring loaded opening device; 2. protechnical cable cutter;
3. liquid helium container; 4. superinsulation; 5. liquid helium
filling port; 6. electrical feedthrough; 7. spiraltron ion detector;
8. chevron baffles; 9. quadrupole mass filter; 10. ion lens;
11. polyimide plunger.

The liquid helium content of the reservoir is about 2.3 liter, for a standing time of about 12 hours. Measured pumping speed is about 1,200 liter/sec. OLSON et al. (1978) have designed a somewhat different cryopump for a balloon-borne ion mass spectrometer; whereas, recently Arnold and colleagues (VIGGIANO et al., 1983) have introduced the use of liquid neon pumps for this kind of experiment. Due to the larger heat of evaporation of liquid neon, such pumps have a much longer standing time and, therefore, a simpler, more lightweight design can be used. However, in order to pump light gases such as H_2, He and Ne efficiently, a charcoal absorption layer must be added to the inside of the cryosurfaces.

On the downward looking input flange of the cryopump, a smaller flange is mounted, electrically, of insulated from the pump body. This allows the application of a draw-in potential to attract ambient ions towards the instrument. A sampling aperture is drilled in the central part of the inlet flange, where thickness is reduced to 0.1 mm. The diameter of the sampling hole is a compromise between two conflicting requirements: maximum ion signal and minimum inside pressure. Most of our data were obtained with a sampling hole of 0.2 mm diameter.

Prior to balloon launching the sampling hole is covered with a polyimide plunger, which can be removed by remote control as soon as the gondola has reached the desired working altitude. This opening system has been described in detail previously (INGELS et al., 1978).

In the configuration of Figure 2, the quadrupole mass filter and ion focussing device are mounted rigidly on the sampling flange to avoid centering problems. In previous flights, quadrupoles having a rod radius of 6.3 mm and a length of about 120 mm have been used (type: Finnigan and Vacuum Generators). OLSON et al. (1978) describe the use of a similar mass filter, although application of smaller quadrupoles (rod diameter = 4.5 mmm) has been reported (ARNOLD and QIU, 1984).

In our setup, the ion focussing device consists of a single cylindrical lens element placed in front of an ionizer delivered by the quadrupole manufacturer. The elements of this ionizer can be put at different potentials, according to whether it is used as an electron impact ionizer or as an element of the ion focussing lens. Switching from lens to ion source configuration can be done by remote control. The ionizer has proven to be very useful for _in situ_ calibration of the instrument, which allowed an unambiguous ion mass determination (ARIJS et al., 1980). At present it is merely used for preflight testing.

Although the use of the ion lens contributes to an increase in the ion signal, it also hampers the expansion of the gas beam, which carries ions through the sampling hole. As a result, a rather high pressure exists just behind the inlet aperture. Since in this region ions are accelerated by electric fields the ion abundance data can be falsified to a high degree by field-induced ion dissociation.

To overcome this ARNOLD and QIU (1984) recently used a configuration where no focussing device was used. Ions were simply guided into the quadrupole by a 50 V potential on the mass filter field axis (pole bias).

After passing through the mass filter, the ions are collected by an ion detector. In view of the lower signal, pulse counting techniques have to be applied and, therefore, an appropriate detector needs to be chosen. In our case a continuous dynode electron multiplier (Spiraltron SEM 4219 – Galileo Optics) was used, although the application of other types (Johnston Laboratories MM-1) was also reported (OLSON et al., 1978).

(b) Electronics Package

The various modules located in the pressurized part of the payload are shown in the block diagram of Figure 3. First there is the lens supply unit, furnishing the electrostatic ion lens and the sampling aperture with appropriate voltages of selectable polarity, referenced respectively to the sampling plat and to the metallic structure. It can operate either in an ion sampling or in an ion source mode, the latter mode only being used during in-flight mass scale calibration or for payload testing.

The quadrupole supply unit produces the RF and DC voltages required to drive the quadrupole mass filter. It is designed so that RF and DC voltages can be controlled independently, allowing a great variety of operating modes. The mass range covered by the quadrupole depends upon the selected RF frequency, the maximum attainable RF voltage, the quadrupole dimensions and the desired mass resolution. In the current payload configuration a mass range from 0 to 330 amu at high resolution is realized with 1500 V peak-to-peak RF excitation at 2 MHz and a quadrupole rod diameter of 6.3 mm.

The spiraltron ion detector, located behind the quadrupole mass filter, requires high voltages, delivered by a separate module. About 3 kV between input cone and anode is needed by the spiraltron for proper operation in the saturated pulse counting mode. Furthermore, the module allows for input cone voltage switching between −3 kV or +1.5 kV, in order to accommodate for positive or negative ion acceleration.
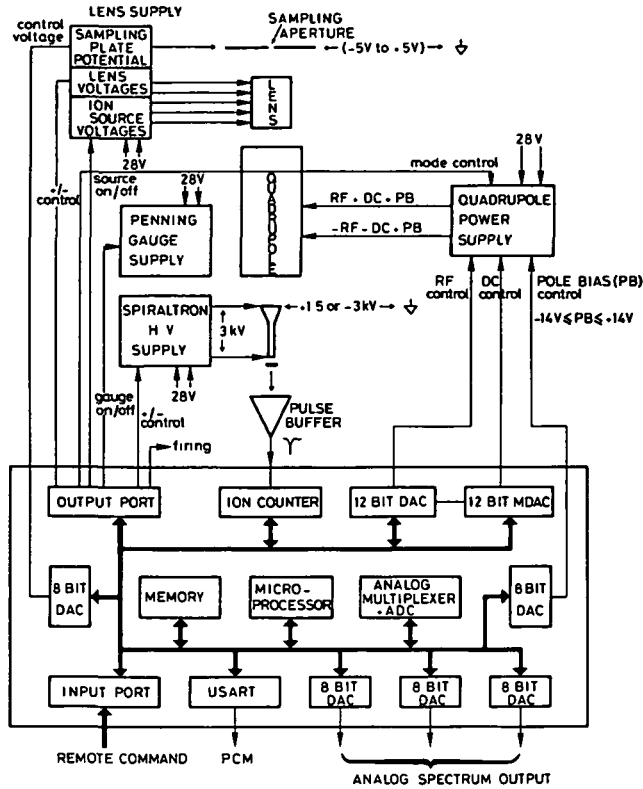
Figure 3. Block diagram of onboard electronics.

In the pulse buffer, which is AC coupled to the anode of the detector, collected charge pulses are converted into voltage pulses with mean amplitudes of a few hundred mV. Instead of using the classical charge amplifier approach, a very simple circuit, based on a high speed, low input capacitance buffer amplifier (NS LH0033), is applied here. The charge cloud leaving the spiraltron is merely integrated on the RC network, formed by the total wiring capacitance (about 20 pf) seen by the anode and by a 1 kΩ leak resistor.

Since collisions with neutrals must be avoided in the mass filter assembly, it must be operated at pressures below about 10^{-4} Torr. Therefore, inside pressure is continuously monitored by a Penning gauge in order to verify the cryopump's operation. Another high voltage unit supplies this gauge with about 2.3 kV. The current consumed by it, which is related to pressure, is measured by a logarithmic electrometer. This value is included in the telemetry format of the payload.

In order to enhance the performance of the balloon-borne mass spectrometer, a microprocessor (INTEL 8080) based control and data management unit has been included in the instrument. The design objectives and its hard- and software implementation have already been described before (NEVEJANS et al., 1982). The unit executes the following main tasks: it controls the polarity of the lens voltage and the spiraltron high voltage; it determines automatically the optimum potential of the sampling aperture; it produces the ramping voltages for the quadrupole supply; it counts the pulses leaving the pulse buffer and stores the

measured values in a spectrum memory; it acquires important parameters of the ambient; it does remote control interpretation and organizes transmission of spectrum and housekeeping data in analog and digital (PCM) formats. All of these duties are governed by software stored in onboard nonvolatile memory. One of the key features of this microprocessor based unit is the selection of an appropriate mass scanning mode. In our instrument, all scan-defining parameters can be optimized: resolution mode, extent of the scan range and number of spectrum channels. Two major resolution modes are implemented (NEVEJANS et al., 1982). The constant resolution mode, wherein ions are filtered with a mass independent, constant, finite resolution ($m/\Delta m$), can be used either to enhance throughput of the mass filter at reduced resolution or to access ion masses, beyond the normal mass range of the instrument. This mode is most often applied during valve controlled balloon flights, when relative abundance profiles of known stratospheric ion species are measured.

An offspring of the constant resolution mode is the integral mode. Here, only RF is supplied to the quadrupole. This results in a shift of the rising edge of all mass peaks towards the low end of the mass scale. Consequently, all mass peaks overlap and, therefore, total ion abundance can be measured at a fixed low level, RF excitation. When the RF voltage is scanned however, the mass filter behaves as a high pass filter.

A second mode is the constant peak-width mode. The resolution ($m/\Delta m$), controlled by the ratio of the DC and RF supply voltage of the quadrupole mass filter, becomes a linear function of mass so that peak-width (Δm) remains constant all over the mass range. The constant peak-width mode is used primarily for the unambiguous determination of mass numbers with a 0.1 to 0.8 amu uncertainty.

(c) Telemetry, Telecommand and Data Reduction

The described assembly of electronic modules is connected to an independent telemetry-telecommand (TM-TC) system. During flights over Southern France a CNES supplied package is used (SITTEL TM-TC), which has nine analog channels (IRIG 5, 6, 7, 9, 11, 12, A, C and E) and a maximum of 27 latching relays (three different addresses with 9 relays each) available to the user. Up to three fully separately powered and integrated mass spectrometers can be interfaced with one such package without any difficulty. Each instrument has then three analog telemetry channels at its disposal: one for the digital serial data stream generated by the on-board microprocessor (PCM rate between 700 and 1300 bits/sec) and two for transmitting analog copies of technological data and mass spectra.

Each mass spectrometer utilizes eight latching relay contacts to form a digital telecommand input and one additional for power on-off switching. The digital information is used by the microprocessor software to select one of the stored measuring programs or to perform service tasks.

The digital data, transmitted over an analog telemetry channel, is handled by a ground borne real-time computer (HP 1000 series), equipped with PCM bit and frame synchronizers (EMR models 720 and 727) and running multitasking software (HP RTE-M III operating system). Housekeeping data about the ambient and internal conditions (pressure, temperatures, voltages, vacuum, etc.) of the payload are displayed and continuously refreshed on a console, while spectrum data are stored on digital tape. The latter data can also be plotted on the console or on a printing plotter.

CALIBRATION OF THE INSTRUMENT

To calibrate the mass scale of our instrument, to check its sensitivity and

to determine the appropriate parameters, which are stored in the memory of the microprocessor control unit, extensive laboratory studies have been performed.

The stratospheric plasma is simulated in a vessel, fitting on the mass spectrometer, by ionizing a nitrogen - nitric oxide gas mixture (typically 1% NO in N_2) with UV irradiation (the 129.6 nm line of a xenon discharge). The pressure of this gas mixture can be stabilized over a wide range (0.1 to 100 Torr) and the ratio NO/N_2 as well as the xenon lamp intensity are kept constant simultaneously.

In this way a reproducible ion population is created having a number density similar to the stratospheric situation, but with a different composition.

The same setup has been used previously (ARIJS et al., 1982a) to investigate the effect of the ion lens field on proton hydrate cluster breakup.

It should be emphasized that so far only relative abundance ratios of different ion species were determined and no absolute ion densities have been deduced from stratospheric ion composition measurements. The derivation of absolute number densities would require a special calibration system, which has not been realized yet, due to the difficulty of independently measuring ion densities.

Another remaining problem is mass discrimination. Since, in most of the present applications of ion composition measurement, moderate resolution spectra have been used, these discrimination effects are believed to be of minor importance. If in the future, however, high resolution spectra will be used, this phenomenon has to be analyzed in the laboratory.

MEASUREMENTS

(a) State of the Art Review

Since 1977 many measurements have been performed with balloon-borne ion mass spectrometer, mainly by two groups (Max Planck Institut fur Kernphysik, Heidelberg and Belgian Institute of Space Aeronomy, Brussels). The results of most of these measurements as well as typical ion spectra have been reported in the literature (see reviews of ARNOLD (1980) and ARIJS (1983) and references cited therein). Therefore, we will only give a concise description of the state of the art and focus more on future advances in the measurement technique, and on problems related to possible misinterpretation of data.

The major positive ions detected in the altitude region 20 to 45 km turned out to be proton hydrates - $H_3O^+(H_2O)_n$ - and nonproton hydrates of the $H^+X_\ell(H_2O)_m$, where X most probably is acetonitrile (CH_3CN) (ARNOLD, 1980; ARIJS, 1983). From the relative ion abundance measurements, the mixing ratio of CH_3CN was derived in the altitude region 45 to 20 km (HENSCHEN and ARNOLD, 1981a; ARIJS et al., 1983a). Although recently an _in situ_ formation mechanism for CH_3CN has been proposed (MURAD et al., 1984), the CH_3CN mixing ratio profiles as deduced from ion mass spectra seem to suggest a release of acetonitrile at the Earth's surface, followed by upward diffusion and destruction by OH in the stratosphere (BRASSEUR et al., 1983).

Apart from the major positive ions, many other positive ions have been detected in the stratosphere (HENSCHEN and ARNOLD, 1981b; ARIJS et al., 1982a). It was shown that the measurements of minor mass peaks offer the possibility of trace gas detection of species such as CH_3OH, NH_3, a.s.o. It should be noted, however, that signal instabilities, which are very pronounced at low ion count rates and possible contamination effects, to be discussed hereafter,

hamper the usefulness of the method as a full grown analytical tool.

The major negative ions observed in the stratosphere are $NO_3^-(HNO_3)_n$ and $HSO_4^-(H_2SO_4)_\ell(HNO_3)_m$ cluster ions (ARNOLD, 1980; ARIJS, 1983).

From the relative ion abundances, both HNO_3 and H_2SO_4 concentration were derived. The derivations of nitric acid vapour mixing ratios, however, are strongly influenced by cluster breakup. The derivations of sulfuric acid ion concentrations, on the other hand, are not subject to these problems and are of great importance for our understanding of the sulfur chemistry and aerosol formation (ARIJS et al., 1981, 1982b, 1983b,d; ARNOLD et al., 1981a, 1982; ARNOLD and BUHRKE, 1983; VIGGIANO and ARNOLD, 1981, 1983; QIU and ARNOLD, 1984). More laboratory data concerning the appropriate ion-molecule chemistry, however, are needed to exploit the data to a full extent.

The detection of minor mass peaks in negative stratospheric ion mass spectra (ARIJS et al., 1982b; MCCRUMB and ARNOLD, 1981) has also opened a way for detecting trace gases so far not measured (such as HCl, HOCl, a.s.o.), but again the same remarks as for positive ions concerning signal instabilities and contamination are valid.

A problem encountered in all in situ analytical techniques and strongly influencing stratospheric ion mass spectrometry data is contamination. It is evident that a technique capable of detecting trace species in the ppt range and lower is extremely sensitive to this problem. It has been established that contamination is mostly influencing the data during measurements obtained in the ascent phase of the balloon flight or at float altitude (VIGGIANO and ARNOLD, 1983; ARIJS et al., 1983a,c). Since contaminants originate from outgassing of the balloon and gondola, the problem is also more acute in daytime measurements. An illustration of the effect of degassing is given in Figure 4, which shows two positive ion spectra obtained by our group at 45.7 km altitude during daytime. Both spectra were recorded at float altitude when the balloon was oscillating between 45.6 and 45.8 km. Spectrum A, containing mass peaks belonging mainly to the natural ions, was obtained during a descending phase of the altitude oscillation, whereas spectrum B was taken during an ascending motion of the payload. It is clear that in spectrum B, contaminants falsify the results considerably. This is explained by the fact that in spectrum B the gondola moves through the wake of the balloon, containing gases released by the balloon and some payload construction materials. These gases are mainly organic vapours, with a high proton affinity and thus are participating in the positive ion chemistry (ARIJS et al., 1983a).

It is also evident that these effects even if not as dramatic as those in Figure 4, may cause misinterpretations, especially in the detection of minor mass peaks.

To overcome these contamination problems, most of the data of our group used so far were obtained at nighttime or during descent in flights with valve controlled balloons. Another remedy which might be envisaged in the future is the use of reel down mechanisms, such as the one recently developed by ANDERSON and HAZEN (1983).

One of the most appealing applications of stratospheric ion mass spectrometry is the detection of trace gases. At present this has been realized by two methods, described to full extent by ARNOLD et al. (1980), namely the steady-state method and the equilibrium method. In the latter one, the partial pressure p(B) of a trace gas B is derived from
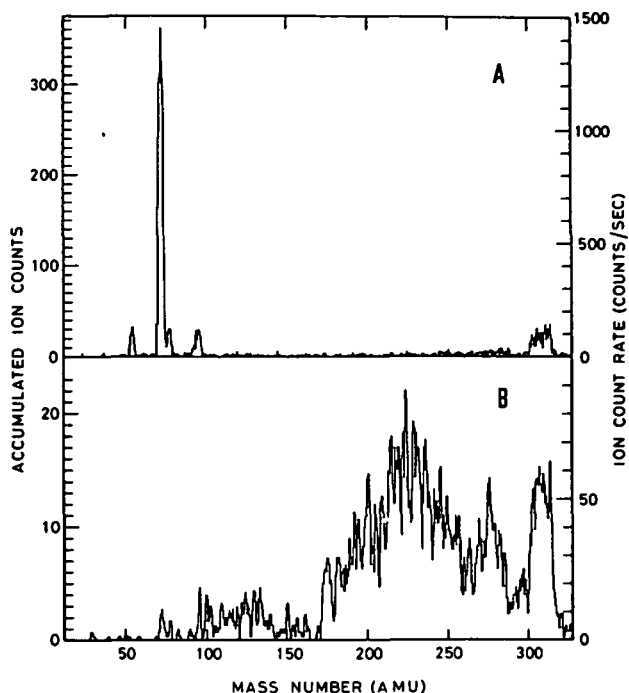
Figure 4. Two typical positive ion spectra obtained around
45 km altitude. Spectrum A is recorded during a descending
motion of the balloon, spectrum B during an ascending motion.

$$p(B) = \frac{[A^{\pm} B_{n+1}]}{[A^{\pm} B_n]} K^{-1}$$

where square brackets denote number densities and K is the equilibrium constant in atm^{-1}. The core ion $A^{\pm}$ can be positive or negative; major core ions observed in the stratosphere are H_3O^+, H^+CN_3CN, NO_3^- and HSO_4^-. The main ligands B detected are H_2O, CH_3CN for positive ions and HNO_3 and H_2SO_4 for negative clusters. For some cluster families, such as $H_3O^+(H_2O)_n$ and $NO_3^-(HNO_3)_{\ell}$, equilibrium constants are known from laboratory measurements and thus p(B) can be derived from the ratio of the fractional ion abundances.

In general, however, the ligands B are weakly bound to the core ions. Immediately behind the sampling aperture of the mass spectrometer, where ions are accelerated by the focussing lens or by the field axis potential of the quadrupole and where pressure is still rather high, the charged particles make many collisions with neutral gas molecules. As a result, field-induced collisional dissociation of a fraction of the ions occurs and some of the ligands B are "boiled orf." Therefore, the measured fractional ion abundance ratio can differ substantially from reality.

A typical example of such measurements is shown in Figure 5, where we have plotted the ratio $H_3O^+(H_2O)_3/H_3O^+$ as measured in a balloon flight performed with a 1,000,000 m^3 Winzen balloon on 23 September 1982 over Southern France.
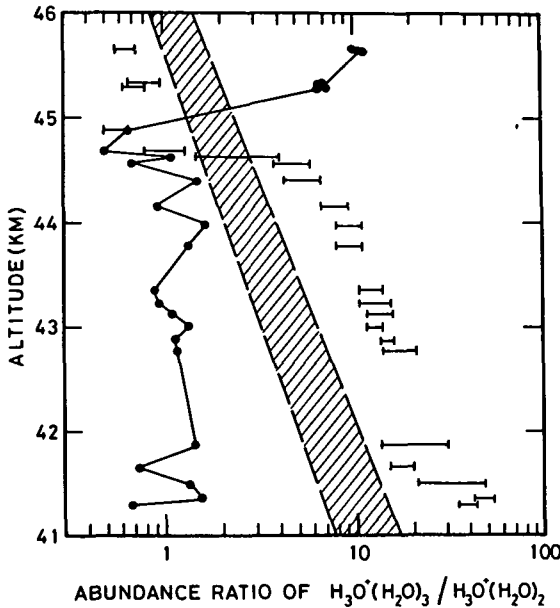
Figure 5. Relative abundance ratio of signal at
mass 73 to signal at mass 55 as measured in
a high altitude balloon flight.

For comparison, we have also shown the ion abundance derived by

$$[H_3O^+(H_2O)_3]/[H_3O^+(H_2O)_2] = K[H_2O]$$

and

$$- RT \ln K = \Delta H - T\Delta S$$

where the values of LAU et al. (1982) were used for ΔH and ΔS and a constant
water vapour mixing ratio of 3 ppm was assumed throughout the whole altitude
region considered here.

The shaded area on Figure 5 represents the results of a calculation for
standard atmosphere temperature conditions (lower limit for summer and upper
limit for spring-fall). Use of the in situ measured temperature profile leads
to the horizontal bars, the width of which is proportional to the temperature
measurement error. As can be seen, the measured ion abundance ratio below 45 km
is much lower than expected, which is due to the dissociation of
$H_3O^+(H_2O)_3$ into $H_3O^+(H_2O)_2$ in the instrument.

Above 45 km the measured ion abundance ratio is larger than expected.
These measurements were taken at float altitude during daytime; whereas the data
below 45 km were recorded during descent, due to the cooling of the balloon
after sunset.

The too-high ion abundance ratio above 45 km is ascribed to contamination,
resulting from balloon and payload outgassing caused by solar heating. One of
the major products of this desorption is water, which causes a shift of the
proton hydrate distribution towards higher masses. The high signal at mass 73
$H_3O^+(H_2O)_3$), responsible for the too high ion abundance ratio, partly
results from cluster breakup of mass 91 ($H_3O^+(H_2O)_4$).

Figure 5 is at the same time a good illustration of contamination and cluster breakup. It should be pointed out that the effect of cluster breakup is strongly dependent on ambient pressure (altitude) and instrument configuration (diameter of sampling hole, focussing potentials a.s.o.) and may, therefore, vary from flight to flight. For the measurements of Figure 5, a sampling hole of 0.4 mm diameter was used.

It is clear that in order to use ion mass spectrometric data for analytical applications, the cluster breakup effects should be avoided or very well understood so that they can be corrected (ARNOLD et al., 1981b; ARIJS et al., 1982a).

In any case, care should be taken in the interpretation of fractional abundance data, especially if they are used for deriving unknown thermochemical values (ΔH and ΔS) of some clustering reactions.

It should be pointed out that the derivation of CH_3CN number densities from positive ion data and of H_2SO_4 vapour concentrations from negative ion measurements are believed not to be influenced by cluster breakup. In these cases, the fractional ion abundances of two distinct ion families (proton hydrates and nonproton hydrates; NO_3^- and HSO_4^- ions) are compared. Cluster breakup only results in a modification of the distribution within the same ion family and is unlikely to cause the conversion from one family to another.

CONCLUSIVE REMARKS

During the past decade considerable progress has been made in the technology of detection and identification of ambient ions in the stratosphere. The measurements performed hitherto have provided an insight in the major processes governing the ion composition in the altitude region 20 to 45 km. To get a more detailed understanding and to exploit the data to a further extent, however, some developments will be necessary. More extensive calibrations of existing instruments are necessary to be able to convert ion count rates to ion number densities, to correct for cluster breakup and to understand possible mass discrimination effects. New instruments or improvements to existing ones need to be developed to avoid cluster breakup and to increase the sensitivity of mass spectrometers. Since the latter is at lower altitudes mainly limited by ion scattering by residual gas molecules in the instrument, more powerful pumping systems will be part of the new developments. On the other hand, the use of other types of mass filters, such as magnetic mass sector instruments and simultaneous detection techniques may open new perspectives. The altitude range of existing measurements need to be extended and the latitudinal variation of ion compositions should be investigated. To extent the altitude range the use of other measurement platforms such as parachute borne rocket payloads, airplane borne instruments (HEITMANN and ARNOLD, 1983) and the use of reel down mechanisms may become necessary. Finally, in order to interpret the data, more laboratory work on the appropriate ion-molecule reactions is urgently needed.

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