DETERMINATION OF THE COMPOSITION OF RARIFIED NEUTRAL ATMOSPHERES BY MASS SPECTROMETERS CARRIED ON HIGH-SPEED SPACECRAFT Professor A. Nier University of Minnesota

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# INTRODUCTION - A. NIER:

As all of you know, mass spectrometers have been used in the laboratory for many years for analyzing mixtures of gases and it has been possible to analyze rather complex mixtures if one has calibrations for the individual gases. There have been dozens of sounding rocket flights which have carried mass spectrometers to the thermosphere region of our atmosphere, and there have been at least a half dozen satellites which have carried mass spectrometers for making analysis of the neutral atmosphere as well as the ionized atmosphere. On the Viking mission there will be two mass spectrometers on each of the landers. One will make measurements in the upper atmosphere and the other will be on the lander itself. The latter will make atmospheric analyses once the lander touches down on the surface and will also look for organic compounds and volatiles in the soil. The Pioneer Venus program will have mass spectrometers both on the entry vehicle and large probe, and on the orbiter. As can be seen, mass spectrometers are playing an important role in the space program, and for good reason, especially in those missions where one doesn't know what is present. Where there are unknown mixtures, there's probably not a more versatile tool than a mass spectrometer. One has enormous dynamic range and can detect very rare constituents in the presence of much more abundant ones. Unlike many methods which may be sensitive for particular classes of compounds, the sensitivity is roughly the same for all compounds.

Today I want to talk about the use of mass spectrometers carried on high speed vehicles through rarified atmospheres. Following what Don Hunten mentioned yesterday, if you are going with a probe to a planet surface, one should take advantage of the opportunity to make measurements as one approaches the planet. Tying measurements in the thermosphere to those in the lower atmosphere provides valuable information concerning atmospheric processes.

Making quantitative measurements with mass spectrometers carried on high speed vehicles poses certain problems. I want to discuss solutions to some which arise as one passes through a rarified atmosphere. Other speakers will discuss measurements in more dense atmospheres.

# THE OPEN SOURCE ATMOSPHERE EXPLORER MASS SPECTROMETER

In our work we have been using magnetic deflection instruments for performing mass analysis. The ion sources are of our own design and the mass analyzer employs the familiar Mattauch-Herzog geometry. Figure 8-1 is a schematic drawing of the instrument we have provided for the Atmosphere Explorer satellites C, D, and E. Ions are produced by an electron beam moving perpendicular to the figure. It is represented by the black dot between the two bar magnets M which collimate the beam.

If the instrument moves to the left, the ambient gas entering the instrument is equivalent to a beam toward the right as shown. For an earth satellite such as Atmosphere Explorer-C the beam consists of a stream of particles having a unidirectional component of velocity of 8.5 km/sec to the right and an omnidirectional component corresponding to a Maxwell-Boltzmann distribution having an average speed of about 1 km/sec. Particles entering the region between the magnets M will be ionized, some directly as they pass through the electron beam, others after they have struck surfaces and are slowed down. Ions formed are accelerated toward the slit  $S_1$ , in part due to a repelling field between Sh and the focusing plates  $J_1$  and  $J_2$ .



In the instrument shown there are two collectors beyond the slits  $S_3$ and  $S_4$ , making possible the simultaneous collection of ions differing in mass by a factor of 8. Mass spectra are swept by changing the total accelerating potential applied to the ions along with the field in the electric analyzer. In the case of missions to comets where the atmosphere is extremely tenuous the two multipliers could be replaced by a channel multiplier array, making possible the simultaneous collection of many masses. A practical instrument such as discussed can be built to weigh 6 kg or less and consume under 5 watts of power.

# MASS SPECTROMETER PERFORMANCE IN HIGH SPEED MOLECULAR BEAMS

Last year (thanks to the cooperation of Prof. J. B. French and his colleagues) we had occasion to test one of our Atmosphere Explorer open source instruments in the high speed molecular beam facility of the Institute for Aerospace Studies of the University of Toronto. Figure 8-2 is a schematic view of the test facility. The high speed beam is produced by the free expansion of a low molecular weight carrier gas (helium in our case) seeded with a small amount of argon and  $CO_2$ , the gases of interest to us in our tests. The mixture leaves the heated ceramic tube through a pinhole as shown to the left in the figure. After passing through a skimming and collimating chamber, the beam impinges on the mass spectrometer attached to the main chamber as shown.

The response of the instrument to different angles of attack could be checked by bending the bellows. When the beam flag was rotated into place, the background in the chamber could be measured. When the stagnation plate was slid into place, the bellows chamber became an idealized stagnation chamber, making possible a check of the extent to which the ion source departed from an idealized closed source.



CurveA of Figure 8-3 os a typical mass spectrum obtained when a 3.9 kg/sec beam impinges on the ion source. One sees peaks corresponding to  $CO_2$  and Ar as well as impurities such as  $O_2$ ,  $N_2$ ,  $H_2O$  and some hydrocarbons. When the beam flag is placed in front of the source, one obtains curve B, corresponding to the background in the chamber due to impurities present in the system as well as the scattered molecular beam. As can be seen, for beam particles the background accounts for only about 20 percent of the readings. It is interesting to note that for  $O_2$ ,  $H_2O$  and the hydrocarbon impurities the A and B curves coincide, showing that these gases are due entirely to impurities in the chamber, none being present in the beam.

From a comparison of the A-B difference and the spectrum obtained when the stagnation plate was in place while the flag covered the source, it was possible to show that for Ar and CO<sub>2</sub> the ion source itself behaved as if it were 96 percent stagnated. In other words, the laboratory measurements predicted that the source as designed, when exposed to an ambient atmosphere of heavy gases, would give essentially the same readings as an ideally closed source with a knife-edged orifice. For helium the readings were somewhat lower, showing that this light gas is not completely accommodated upon collision.

# MASS SPECTROMETER PERFORMANCE IN FLY-THROUGH MODE

The availability of the high speed molecular beam made possible tests not previously undertaken. In particular, if grid 3 and the focusing plates  $J_1$ and  $J_2$  are tied to the assembly Sh, there is no field drawing ions out of the region where they are formed, and the instrument is in the retarding potential, or fly-through mode. In this case, incoming gas molecules which strike the ion source and are accommodated have only the energy characteristic of the ion source surface temperature, a few hundredths of an electron volt. On the other hand, those particles which have not struck surfaces have an energy characteristic



of their velocity in the beam, about 0.09 eV per atomic mass unit of mass for a 3.9 km/sec beam. This initial energy is enough to permit them to pass into the accelerating region after being ionized by the electron beam. In other words, in the fly-through mode the instrument, when carried on a high speed spacecraft, has the capabilities of distinguishing between true ambient particles and ones which have hit the instrument's surfaces and become thermalized or altered in nature.

Figure 8-4 shows spectra corresponding to those shown in Figure 8-3 obtained when the instrument was in the fly-through mode. It is interesting to note that except for the 12, 16 and 28 peaks the background curve  $F_B$  is zero, showing that the instrument indeed discriminates sharply against particles which do not have the energy of the beam. The fact that the background at 12, 16 and 28 is not zero comes about because these peaks are fragment ions produced by the dissociation of the background  $CO_2$ . In the ionization process they acquire kinetic energy. Hence these fragments are not excluded. The 14 peak is due entirely to background  $N_2$  in the chamber and as in the case of the  $CO_2$  fragments, acquires kinetic energy in the dissociation and ionization process. As will be discussed later, ambiguities due to the energetic fragments can be eliminated.

The beam tests just discussed were conducted in time to include the flythrough feature in the instrument carried on Atmosphere Explorer-C launched in December 1973.

# APPLICATION OF FLY-THROUGH FEATURE TO ATMOSPHERE EXPLORER MEASUREMENTS

The determination of the absolute densities of atomic and molecular oxygen by mass spectrometers carried on sounding rockets and satellites has been the subject of some controversy. In the case of open source instruments carried on rockets, it was recognized that atomic oxygen was lost by reactions with instrument



surfaces but the extent of the loss was not clear. In the case of closed source mass spectrometers carried on satellites, it was found that after several orbits all of the atomic oxygen was converted to molecular oxygen by reactions on the walls of the cavity enclosing the source. While this made possible the quantitative measurement of atomic oxygen at high altitudes where ambient molecular oxygen was negligible, the method merely gave total oxygen in the interesting region of the atmosphere where atomic and molecular oxygen have comparable abundances.

As has already been mentioned, in its normal mode of operation the Atmosphere Explorer open source mass spectrometer performs essentially as a closed source instrument. In this mode it gives quantitative values for number densities of  $N_2$ , Ar, He and total oxygen. When switched to the fly-through mode, it distinguishes between atomic and molecular oxygen, giving absolute number densities for each. Figure 8-5 illustrates the performance in this mode. The mode is particularly applicable when the spacecraft is spinning at its normal spin rate of 1 revolution per 15 seconds and the instrument is set to toggle back and forth between masses 16 and 32 rather than look at a large number of masses.

Multiplier counts are accumulated for 1/16 sec while the instrument is set to collect mass 16. It then counts mass 32 ions for 1/16 second, switches back to mass 16 for 1/16 second, etc. The results are shown for two different altitudes of orbit 912 as the instrument passes through the forward looking direction as the spacecraft spins. Particle densities are roughly proportional to count rates.

The figure illustrates a number of interesting points: (1) the 16 peak is always greater than the 32 peak at the same altitude, as it indeed should be in the altitude range shown, (2) in going from 179 to 259 km the 32 peak falls



off very much faster than the 16 peak, as it should due to the large difference in scale heights, (3) the background of a few percent of the peak values near the "forward" direction is due primarily to incomplete rejection of slow particles. By operating the instrument with low electron accelerating potentials, 25 volts in our case, the production of energetic fragment ions such as 0 from  $0_2$  is reduced. Since they are made from  $0_2$  produced in part by chemistry in the source, they do not contribute to the sharp peak when the instrument looks forward, and merely add to the background, (4) while part of the width of the peaks is due to the finite acceptance angle of the instrument, the largest part is caused by the fact, which was mentioned earlier, that the "beam" seen by the instrument has a unidirectional component having the spacecraft velocity of 8.5 km/sec and an omnidirectional component of roughly 1 km/sec average velocity corresponding to the Maxwell-Boltzmann distribution at the thermospheric temperature of about 900°K. As the spacecraft spins, particles can thus enter over an angle of a number of degrees. It is interesting to note that at half height the width of the 16 peak is approximately 2 1/2 wider than the 32 peak, as it should be because of the difference in average Maxwell velocities of the two species in the atmosphere. It appears that with proper calibration, the width of the peaks can be used to deduce in situ atmosphere temperatures.

Figure 8-6 gives the plot of peaks such as shown in Figure 8-5 as a function of altitude, and from the relative scale heights provides additional proof that the peaks as read in the fly-through mode are indeed due to the ambient atmosphere uncontaminated by wall collisions effects. The count rates are reduced to ambient number densities through laboratory calibrations supplemented by calibrations in orbits where fly-through readings are interspersed with readings in the normal mode.



# CONCLUSIONS

In a properly designed open source mass spectrometer one can operate in both a "normal" mode and in a mode in which particles arising from collisions with instrument surfaces are excluded. In instruments carried on high speed spacecraft such as will be sent to the unknown atmospheres of other planets or comets this feature is of considerable importance in making a distinction between the true ambient atmosphere and gases which arise as the result of chemical reactions on instrument surfaces.

An example is given in which atomic and molecular oxygen are distinguished by the open source mass spectrometer carried on the Atmosphere Explorer-C satellite.