

SIDAMS:

CEE contract STEP-0009-M(A)

(Simultaneous Ion detection in Atmospheric Mass Spectrometry)

TRACE GAS DETECTION THROUGH PASSIVE AND ACTIVE ION MASS SPECTROMETRY USING A NEW TYPE OF BALLOON BORNE MASS SPECTROMETER.

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1. INTRODUCTION

It has been fairly well established now that heterogeneous reactions on Polar Stratospheric Clouds (PSC) particle surfaces and denitrification play a primary role in the ozone depletion processes that occur at polar latitudes [1]. Although recent measurements of nitric acid vapour in the winter arctic stratosphere have given evidence for the coupling of PSC formation and denitrification [2], our understanding of the processes leading to the ozone destruction is far from complete. Further continuous in-situ probing of trace gases such as nitric oxides, HNO₃, water vapour and H₂SO₄ (which is a precursor for the condensation nuclei of PSC's) in the winter polar stratosphere will therefore remain an essential part of the required scientific effort. With these objectives in mind a collaborative effort is undertaken between the Belgian Institute for Space Aeronomy, the Physikalisches Institut of the University of Bern and the Laboratoire de Physique et Chimie de l'Environnement of the CNRS to develop a new balloon borne instrument capable of measuring the trace gases mentioned above by ion mass spectrometry techniques.

2. PASSIVE CHEMICAL IONIZATION TECHNIQUE

The passive chemical ionization method allows the detection of trace gases through the steady state method and the thermodynamic equilibrium method. The former is based on the selective reactivity of atmospheric ions with some trace gases, leading to characteristic product ions. Assuming that the ions disappear only by ion-ion recombination and knowing the appropriate ion-molecule reaction rate coefficients, the number density of trace gases involved in the ion-molecule reaction chain can be derived from the measured abundance ratio of primary and product ions in the spectra of the ambient ions. In this way the concentration profiles of CH₃CN and H₂SO₄ have been derived from the positive and negative ion spectra respectively in the altitude range from about 20 to 45 km.[3]

Although the method is very sensitive (mixing ratios down to the ppt range can be derived) it is limited to those trace gases which react with ambient cluster ions. Furthermore collision induced dissociation (CID) in the sampling region of the mass spectrometer can lead to spurious decrease of product ions before mass filtering and thus to false results.[4]

The thermodynamic equilibrium method relies upon the fact that some ambient ions undergo association reactions with some natural trace gases and form families of cluster ions with the same core ion but with a different number of ligands of

the same molecule. Typical examples are the $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ and the $\text{NO}_3^-(\text{HNO}_3)_n$ clusters. From the knowledge of the equilibrium constant of the association reactions and the temperature, the partial pressure of the trace gas involved can be derived if the relative population of a cluster ion family is measured by ion mass spectrometry. Unfortunately this method is even more sensitive to CID and the HNO_3 mixing ratios obtained with it so far are only valid above 30 km altitude.[5]

3. THE INSTRUMENT

Based upon the foregoing considerations and previous experience obtained with balloon borne quadrupole ion mass spectrometers the following requirements were formulated for the new instrument:

- higher sensitivity
- increased mass resolution and
- lower CID effects upon ion sampling.

The heart of the instrument which is presently under development and which we expect to satisfy the requirements mentioned above is shown in figure 1.

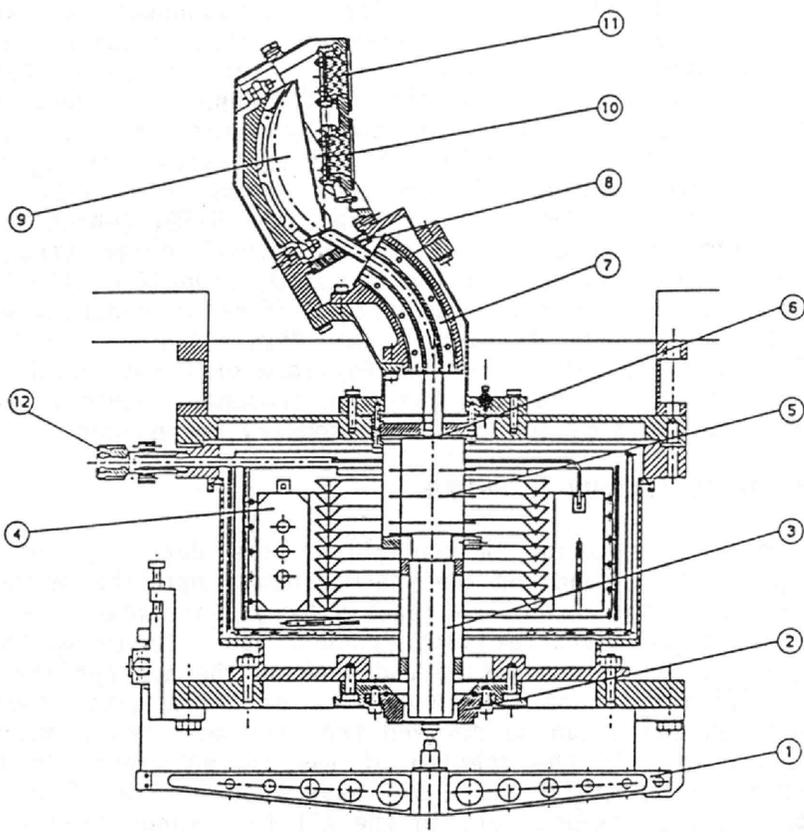


Fig. 1 - Cross section of high vacuum part of the mass spectrometer.

- 1) spring loaded opening device;
- 2) ion inlet plate;
- 3) octopole ion transfer;
- 4) liquid helium container;
- 5) ion lens system;
- 6) ion inlet slit;
- 7) toroidal electrostatic deflector;
- 8) ion guard;
- 9) permanent magnet;
- 10) microchannel plate;
- 11) fiberoptics seal;
- 12) liquid helium filling port.

A fully detailed description of the new mass spectrometer has already been given elsewhere [6]. In principal the instrument consists of:

- a modified Mattauch-Herzog mass analyser having a mass range of 12 to 500 amu, in which the ions are mass separated by a combination of a toroidal electric field and of constant magnetic field.
- an ion detector, allowing a simultaneous measurement of a selected part of the full mass range and consisting of two 1 inch microchannel plates with a phosphor screen, a fibre optics seal and a linear position sensitive light detector attached to them.
- a high speed cryopumping system which pumps against the leak through which the ions are admitted together with the ambient air and which maintains the vacuum in the mass filter and the detector region.
- a special focussing device which leads the ions to the entrance slit of the Mattauch-Herzog filter by means of an RF octopole field and an electrostatic ion lens. It is the transmission of the octopole, which will actually limit the mass range of the instrument.

Within the SIDAMS project two mass spectrometers will be built: one for positive and one for negative ions. For each instrument one balloon flight is foreseen from the CNES balloon launching base at Aire sur l'Adour (France).

Recent laboratory measurements with the positive ion mass spectrometer have shown that even with a resolution, which is ten times better than the one chosen for our old quadrupole instruments an eightfold increase in sensitivity is obtained. Furthermore it has been found that very small octopole bias voltages can be used (less than 1 V) and therefore minimal CID effects are anticipated.

It is expected therefore that with the positive ion mass spectrometer it will be possible to derive concentration profiles of both CH_3CH and H_2O in the stratosphere by using the passive chemical ionization technique.

From the spectra obtained with the negative ion mass spectrometer, which is under construction, profiles of H_2SO_4 and HNO_3 will be inferred using the same technique.

4. ACTIVE CHEMICAL IONIZATION TECHNIQUE

To extend the capabilities of the instrument an ion source will be added in future, which will allow the application of the active chemical ionization method. The active chemical ionization method [7] relies on the reactions of atmospheric trace gases with ions produced by an external ion source, mounted in front of the mass spectrometer, leading to specific product ions. From the analysis of the relative abundance of the precursor and product ions in the spectra obtained with the ion source, the mixing ratios of the reactive trace gases can be determined.

The innovation of the active chemical ionization technique in the SIDAMS project lies in the fact that an ion source will be developed producing mainly Cl^- or I^- ions. The Cl^- ions produced react both with HNO_3 and N_2O_5 , whereas I^- only reacts with N_2O_5 . Both reactions result in NO_3^- core ions. Since the reaction rate constants of the three ion-molecule reactions involved are known from laboratory measurements [8], the N_2O_5 and HNO_3 concentrations can be inferred from the abundance ratios $[\text{NO}_3^-]/[\text{Cl}^-]$ and $[\text{NO}_3^-]/[\text{I}^-]$ measured with the ion mass spectrometer.

5. STATUS OF THE PROJECT

The project described in the foregoing paragraphs is financed by the CEC through the contract STEP-009-M(A) for a period of two years. The activities foreseen within this contract are:

- construction of a positive and negative ion mass spectrometer

- 2 balloon flights from Aire sur l'Adour to test the performance of the mass spectrometers for the passive chemical ionization technique

- development of the ion sources

Presently the mechanical hardware of the positive ion mass spectrometer is practically finished and its electronics and software are in a final stage.

The first balloon flight is scheduled in the Spring of 1991.

Some parts of the negative ion mass spectrometer are already under construction and the flight with this instrument is foreseen in Autumn 1991.

The ion source is under development and several laboratory tests have been done. If the instrument is ready in time and the results of the first flights are satisfactory, it will be used for the participation of our team in the European Winter Arctic Campaign in 1991-1992.

6. REFERENCES

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