SIDAMS *-ATMOSPHERIC TRACE GAS MASS SPECTROMETRY WITH SIMULTANEOUS ION DETECTION

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The aim of the research within this project, partly financed by the Commission of European Communities within the STEP programme, is to measure in-situ the positive and negative stratospheric ion composition simultaneously with a new second generation balloon borne ion mass spectrometer offering higher mass and spatial resolution, an increase in absolute sensitivity and reduced fragmentation of complex ions. This technique has the capability to determine in-situ the concentration of various stratospheric trace gases, by using passive or active chemical ionization methods.

The passive chemical ionization method is based upon the analysis of the abundances of the natural ions as measured with an ion mass spectrometer in the stratosphere. From the knowledge of the ion chemistry which gives rise to the formation of these ions (ionization rate by cosmic rays, primary Nd_2^+ and O_2^+ ions formed by the cosmic rays into the terminal ions and ion-ion recombination) the concentration of the trace gases playing an active role in the stratospheric ion chemistry can be derived.

Presently available stratospheric ion mass spectra exhibit a great variety of species. These have not yet all been studied due to the lack of sensitivity of existing mass spectrometers. The new development proposed here should allow the exploitation of this wealth of information through sensitivity increase.

One of the objectives in a later stage, will be the use of the instrument in the lower stratosphere for the simultaneous in-situ measurement through the active chemical ionization method of $N_2\ O_5$ and HNO_3, traces gases playing

* SIDAMS is the acronym for : Simultaneous Ion Detection in Atmospheric Mass Spectrometry.

an important role in the ozone problem. In the active chemical ionization method an ion source is mounted in front of the mass spectrometer and the artificially created ions react selectively with some trace gases to form product ions, which are together with the precursor ions measured by the mass spectrometer. From the abundance ratio of precursor to product ions, the reaction rates of the conversion reactions and the flight time of the ions from the ion source to the mass spectrometer, the number density of the reactive trace gases can be inferred. This method has been used by another research group to determine HNO_3 vapour concentrations in the stratosphere with an ion source producing mainly CO_3^- cluster ions and exploiting the reaction of these ions with nitric acid vapour. In this project, an effort, will be made for the development of an ion source, which in a later stage will be installed in front of the ion mass spectrometer, and which produces alternatively Cl^- and I^- ions in flight. The use of such an ion source will allow the simultaneous measurement of HNO_3 and N_2O_5 in the lower stratosphere, because Cl^- reacts with both HNO_3 and N_2O_5 whereas I^- only reacts with N_2O_5.

In a first phase however the new instrument will be used for measuring positive and negative ambient ions and trace gases such as H_2O, CH_3CN, HNO_3 and H_2SO_4. The method allows measurements at any time of the day and includes the promise of detection of other trace gases (such as HCl and possibly others).

To achieve the above objectives, a new type of ion mass spectrometer will be used. This instrument, which has now been developed for positive ions in a collaborating effort between the partners involved in this project, consists of a double focussing magnetic mass analyzer followed by a simultaneous ion detection system.

The newly developed mass spectrometer should have a much higher sensitivity than quadrupole instruments used for similar applications, which should result in several benefits, such as :

— for measurements of natural ions in the stratosphere, lower ion focussing fields can be used and the problem of cluster break up or collisional induced dissociation can be avoided. In this way concentrations of trace gases, such as H_2O, CH_3CN, HNO_3 *and* H_2SO_4, as derived from natural ion composition data will be more reliable and accurate.

— for measuring artificially created ions using a suitable external ion source and allowing the detection of other trace gases (active chemical ionization), the observation of mass peaks due to natural isotopes will be very helpful in identifying the ions and the higher sensitivity will allow a much better altitude resolution of the inferred altitude profiles. The newly developed ion mass spectrometer for positive ions has been flown into the stratosphere by means of a stratospheric balloon from the balloon launching center of the CNES in Aire sur l'Adour (S. France) on May 21, 1991. This flight, which was of

merely technological nature showed that the instrument worked well from the technical point of view. High resolution spectra of positive ions were obtained between 20 and 32 km altitude, but signal strength was lower than expected. Laboratory tests are being performed now to look for the reasons of this. The negative ion mass spectrometer is presently being constructed and laboratory investigations are now performed to test several type of ion sources for the active chemical ionization method.