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during the map globus 1983 campaign

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B E L G I S C H I N S T I T U U T V O O R R U I M T E - A E R O N O M I E

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## FOREWORD

This text will be published with the other results of the MAP Globus 1983 campaign, in a special issue of "Planetary and Space Science".

## AVANT-PROPOS

Ce texte sera publié avec les autres résultats de la campagne MAP Globus 1983, dans une édition spéciale de "Planetary and Space Science".

## VOORWOORD

Deze tekst zal verschijnen te samen met de overige resultaten van de MAP Globus 1983 campagne, in een speciaal nummer van "Planetary and Space Science".

## VORWORT

Dieser Text wird veröffentlicht werden zusammen mit den übrigen Ergebnisse der MAP Globus 1983 Kampagne, in einer speziellen Ausgabe von "Planetary and Space Science".

ACETONITRILE AND SULFURIC ACID CONCENTRATIONS DERIVED FROM ION  
COMPOSITION MEASUREMENTS DURING THE MAP GLOBUS 1983 CAMPAIGN

by

J. INGELS, D. NEVEJANS, P. FREDERICK and E. ARIJS

Abstract

Acetonitrile volume mixing ratios are derived from positive ion spectra obtained with a balloon-borne quadrupole mass spectrometer in an altitude region from 21 to 32 km. Comparison of the results with data obtained in previous flights, suggests a larger deviation from reference profiles, probably due to temporal transport phenomena.

From negative ion spectra obtained during the same balloon flight, the concentration of sulfuric acid vapour between 22 and 32 km is also deduced. These results seem to be in reasonable agreement with earlier data which were mostly obtained shortly after a period of enhanced volcanic activity.

## Résumé

Les rapports de mélange d'acétonitrile ont été déduits des spectres des ions positifs mesurés entre 21 et 32 km à l'aide d'un spectromètre de masse quadrupolaire à bord d'une nacelle stratosphérique. Une comparaison des résultats obtenus pendant des vols antérieurs, suggère une déviation plus grande des profils de référence, probablement à cause de phénomènes de transport temporaires.

La concentration d'acide sulfurique a été déduite des spectres des ions négatifs, obtenus pendant le même vol entre 22 et 32 km. Les résultats sont comparables à des résultats antérieurs, obtenus après une période d'activité volcanique augmentée.

## Samenvatting

De mengverhoudingen van acetonitrile werden afgeleid uit de spectra van positieve ionen, gemeten met een ballongedragen quadrupolaire massaspectrometer op hoogten tussen 21 en 32 km. Een vergelijking van deze resultaten met de resultaten bekomen tijdens vroegere ballonvluchten, wijzen op een grotere afwijking van de referentieprofielen, waarschijnlijk te wijten aan een tijdelijk transportverschijnsel.

Uit spectra van de negatieve ionen, gemeten tijdens dezelfde ballonvlucht, werden ook de concentraties van zwavelzuur afgeleid tussen 22 en 32 km. De resultaten zijn vergelijkbaar met vroegere resultaten, die bekomen werden kort na een periode van verhoogde vulkanische activiteit.

## Zusammenfassung

Mischungsverhältnisse des Methanzyanides werden deduziert von positiven Ionenspektren gemessen im Höhenbereich zwischen 21 und 32 km, mit einem Ballongetragenen quadrupolaren Massenspektrometer. Ein Vergleich mit den Ergebnissen von früheren Ballonflügen, suggeriert eine grössere Abweichung der Referenzprofilen, wahrscheinlich durch zeitliche Transportphänomenen.

Schwefelsäurekonzentrationen werden deduziert von negativen Ionenspektren, gemessen im Höhenbereich zwischen 22 und 32 km, während desselben Ballonflug. Diese Ergebnisse sind vergleichbar mit früheren Ergebnissen, bekommen kurz nach einer Periode von erhöhter vulkanischer Aktivität.

## 1. INTRODUCTION

Since the first identification of stratospheric ions, realized with balloon-borne instruments in 1977 (Arijs et al., 1978; Arnold et al., 1978), considerable advance has been made in the field of balloon-borne ion mass spectrometry.

Whereas the first experiments were carried out at a single altitude, progress in ballooning technology has allowed an extension of the measurements in an altitude region from about 20 to 45 km. A simultaneous development of more sensitive, high resolution instruments also resulted in a more definite identification of positive and negative stratospheric ions and a determination of more detailed height profiles of the ion composition (for overviews of recent results, see Arnold, 1980, 1982; Ferguson and Arnold, 1982; Arijs, 1983; Arijs et al., 1984).

The main findings are summarized hereafter. For positive ions, two major families were detected : the proton hydrates (PH) i.e. ions of the form  $H^+(H_2O)_n$  and the so-called non proton hydrates (NPH) of the form  $H^+(CH_3CN)_m(H_2O)_n$ . A study of ion abundances based on steady state considerations and explained hereafter, allowed the derivation of a mixing ratio profile of  $CH_3CN$  between 20 and 45 km. For negative ions, two major groups were found also; one consisting of clusters with  $NO_3^-$  as core ion and  $HNO_3$  as a ligand and another with  $HSO_4^-$  as core ion and with  $HNO_3$  and  $H_2SO_4$  as ligands. A steady state method analogous to the one for positive ions resulted in the derivation of  $H_2SO_4$  concentration profiles. This is an important result, as it provided the first estimations of the concentration of  $H_2SO_4$ , a trace gas important in aerosol formation processes.

Furthermore it has been shown previously (Arnold et al., 1980; Arijs et al., 1981) that negative ion composition measurements may lead to an independent determination of  $HNO_3$  mixing ratios in the atmosphere.

Originally this was one of the main motivations to include stratospheric ion composition measurements in the MAP Globus 1983 campaign. Although this objective proved difficult to meet due to problems with cluster break-up (Arnold et al., 1981; Arijs et al., 1985), the ion mass spectrometer gondolas remained integrated in the MAP Globus 1983 campaign, because they can provide important information on other trace gases such as  $\text{CH}_3\text{CN}$ , a longlived species that may be useful as a tracer for transport problems and  $\text{H}_2\text{SO}_4$ , the chemistry of which is closely related to aerosols, studied by other methods during this campaign (mainly by LIDAR).

## 2. EXPERIMENTAL METHODS AND MEASUREMENTS

The stratospheric ion spectra presented here, were recorded over southern France on 18 September 1983 during our flight S-83 with gondola G7 of the MAP Globus 1983 campaign. A  $100,000 \text{ m}^3$  valve-controlled balloon, type 100 SF Zodiac, was launched at 13:11 U.T. from the CNES base near Aire-sur-l'Adour (approx.  $44^\circ\text{N}$ ,  $0^\circ\text{W}$ ), and a ceiling altitude of 32.2 km (7 mbar) was reached. Between 18:18 and 21:31 U.T., balloon and gondola descended at a rate of about  $1.1 \text{ m s}^{-1}$  from float altitude down to 20.0 km (52 mbar). The payload consisted of our quadrupole ion mass spectrometer QMS2 and an instrument to study aerosol properties by earth limb photography (Ackerman et al., 1981). Total weight of the scientific instruments was 311 kg.

Our QMS2 instrument basically consists of a quadrupole mass filter and a Spiraltron detector (type Galileo Electro Optics secondary electron multiplier 4219) in a high speed liquid helium cryopump, and the appropriate electronic modules. Microprocessor controlled operation guarantees a flexible system, allowing both positive and negative ion sampling with the same instrument. A detailed description of these parts is given elsewhere (Ingels et al., 1978; Arijs et al., 1980; Nevejans et al., 1982; Nevejans et al., 1985).



Stratospheric ions and neutral gases are sampled through a small hole of 0.25 mm diameter in a stainless steel flange of 0.1 mm thickness into a liquid helium cryopump. Behind the inlet hole, neutral gases are pumped and ions are focused into the quadrupole filter by an electrostatic lens, where the polarity of applied voltages is simply inverted between positive and negative ion modes. The high pumping speed of the cryopump ( $1,150 \text{ l s}^{-1}$ ) assures a pressure below  $10^{-4}$  mbar throughout the altitude range covered. The sampling flange is insulated from and biased with respect to the gondola structure with a draw-in potential adjustable between - 5 and + 5 V. This draw-in potential is set for a maximum signal either by remote or by automatic control. After mass filtering, the ions reach the high gain spiraltron detector, signals of which are treated by pulse counting techniques. The cone of the spiraltron is kept at - 3 and + 1.5 kV for positive and negative ions respectively, resulting in an adequate detection efficiency. Mass range and sensibility of the mass filter both depend upon resolution, determined by the ratios of DC and RF voltages applied to the quadrupole rods. In our instrument, resolution can be programmed by the on-board microprocessor. To record the present spectra, a moderate resolution mode ( $M/\Delta M \approx 17$ ) was sufficient, to resolve properly the major mass peaks and to determine the fractional abundances of the major ions in a mass range from 0 to 330 AMU.

The spectra of stratospheric positive and negative ions discussed in this paper were recorded during nighttime, in the descent phase of the flight, to minimize contamination through gases desorbing from balloon and gondola (Arijs et al., 1983). For the same reasons, the distance between balloon and gondola was kept at 170 m. Ambient pressure was measured in flight with a Baratron precision absolute capacitance manometer and temperature was recorded through use of bead thermistors mounted on an aluminium boom of about 1 m.

### 3. RESULTS AND DISCUSSION

#### 3.1. Positive ions and acetonitrile mixing ratios

Although typical ion spectra obtained with our instruments were shown before (Arijs et al., 1982, 1983a, 1983b), it is worthwhile to give a typical positive ion spectrum as recorded in this flight in Figure 1. In this figure, the presence of PH with mass numbers 55 and 73 is obvious, as well as that of NPH mass peaks. A list of observed mass numbers and their identification is given in Table 1.

All positive ion spectra of flight S-83 were obtained with the same moderate resolution ( $M/\Delta M \approx 17$ ). Due to earlier high resolution data (Arijs et al., 1980) such a resolution still allowed identification of the major ions. It also permitted a determination of the ion abundances without having to correct for possible mass discrimination effects on the quadrupole transmittance.

The ion abundances derived from Figure 1 are somewhat different from those of earlier spectra obtained at the same altitude. The most abundant NPH here is mass 78 in contrast to earlier data, where it was mass 96. This fact suggests a greater influence of cluster break-up effects in the present flight data, although sampling conditions (inlet hole diameter, draw-in potential, focus lens elements potentials) were very similar to those used in earlier flights.

It is however unlikely that these cluster break-up effects would result in conversion of NPH to PH, because the  $\text{CH}_3\text{CN}$  ligand is more strongly bound to the core ion than the  $\text{H}_2\text{O}$  ligand, due to its higher proton affinity. Therefore, the ion abundances can still be used to determine  $\text{CH}_3\text{CN}$  mixing ratios,  $\mu(\text{CH}_3\text{CN})$ , as explained before (Arijs et al., 1983a) with a method based on the steady state equation :

$$k_1 \mu(\text{CH}_3\text{CN}) [\text{M}] [\text{PH}] = \alpha [\text{n}^-] [\text{NPH}] \quad (1)$$

Table 1 : Observed major positive ions and tentative identification.

Mass number (AMU)	Formula
55	$\text{H}^+(\text{H}_2\text{O})_3$
60	$\text{H}^+(\text{CH}_3\text{CN})\text{H}_2\text{O}$
73	$\text{H}^+(\text{H}_2\text{O})_4$
78	$\text{H}^+(\text{CH}_3\text{CN})(\text{H}_2\text{O})_2$
83	$\text{H}^+(\text{CH}_3\text{CN})_2$
96	$\text{H}^+(\text{CH}_3\text{CN})(\text{H}_2\text{O})_3$
101	$\text{H}^+(\text{CH}_3\text{CN})_2\text{H}_2\text{O}$
119	$\text{H}^+(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})_2$
142	$\text{H}^+(\text{CH}_3\text{CN})_3\text{H}_2\text{O}$

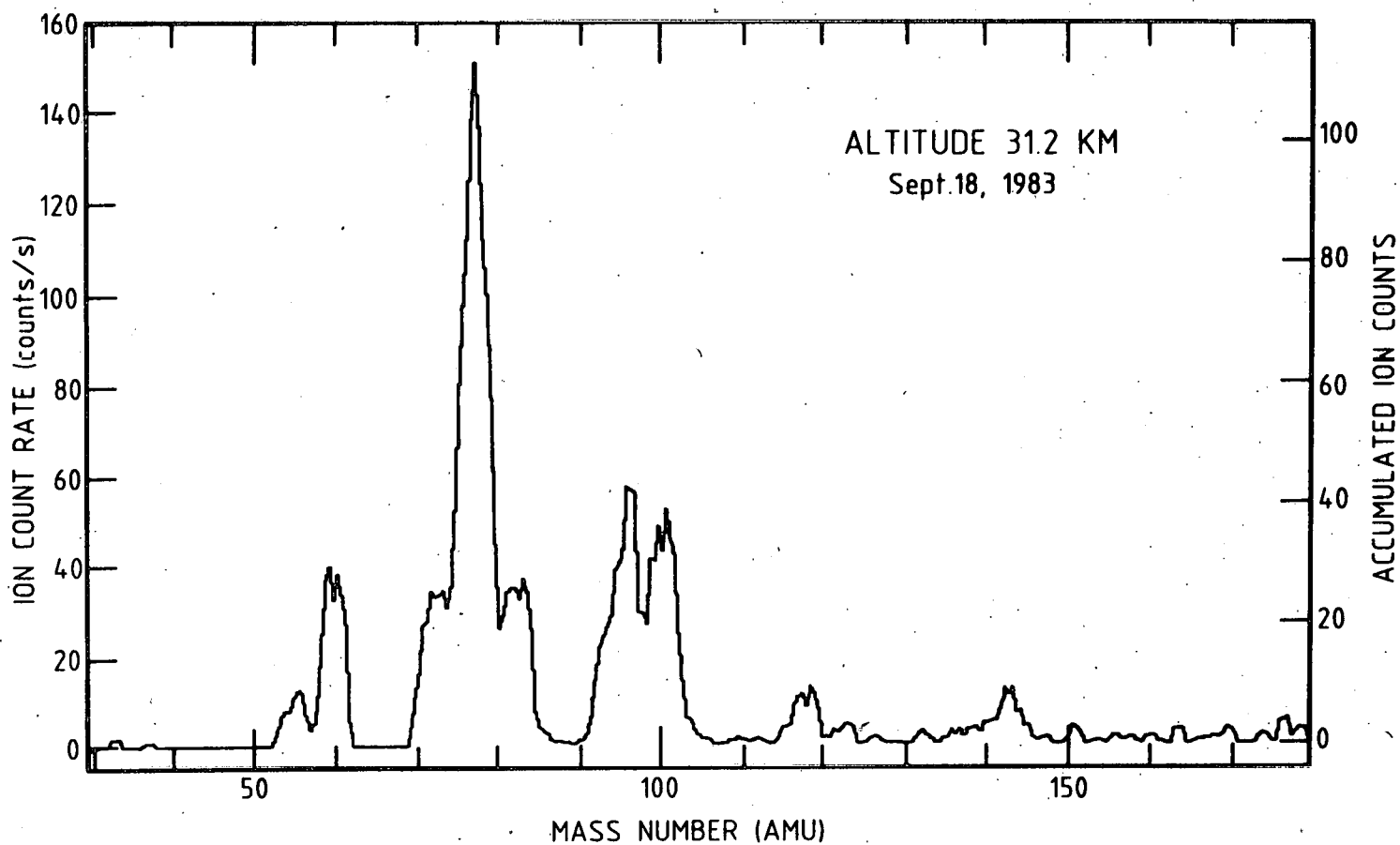


Fig. 1.- Typical positive ion spectrum at an altitude of 31.2 km during flight S-83 or gondola G7 of the MAP Globus 1983 campaign. The integration time for the accumulated counts is 0.75 s.

In this equation the symbols are :

$k_1$  = reaction rate constant for the conversion of PH to NPH in  $\text{cm}^3 \text{s}^{-1}$ ,  
 $[M]$  = total neutral atmospheric density in  $\text{cm}^{-3}$ ,  
 $[PH]$  = total concentration of all PH ions in  $\text{cm}^{-3}$ ,  
 $\alpha$  = ion-ion recombination coefficient in  $\text{cm}^3 \text{s}^{-1}$ ,  
 $[n^-]$  = total negative ion concentration in  $\text{cm}^{-3}$ ,  
 $[NPH]$  = total concentration of NPH ions in  $\text{cm}^{-3}$ .

For calculating the mixing ratios of  $\text{CH}_3\text{CN}$ ,  $\mu(\text{CH}_3\text{CN})$ , a value for  $k_1$  of  $3 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}$  as reported by Smith et al. (1981) was used. The total ion concentration  $[n^-]$  was deduced from a parametrization of Heaps (1978) and for  $\alpha$  the expression (Arijs et al., 1983a)

$$\alpha = 6 \times 10^{-8} \left( \frac{300}{T} \right)^{\frac{1}{2}} + 1.25 \times 10^{-25} [M] \left( \frac{300}{T} \right)^4 \quad (2)$$

was used, where  $T$  is the temperature in K. The mixing ratios of  $\text{CH}_3\text{CN}$  can be calculated with formula (1) if we assume that the height of a mass peak is proportional to the corresponding ion abundance. The results are represented by full circles labeled BISA in Figure 2 and the corresponding mixing ratios of  $\text{CH}_3\text{CN}$  are given in Table 2. For the present data,  $[M]$  was derived from a measurement of ambient pressure and temperature, performed on the gondola.

The shaded area in Figure 2 results from drawing an envelope E for all extant measurements of  $\mu(\text{CH}_3\text{CN})$  apart from three extreme results and the data of this MAP Globus 1983 campaign (Arnold et al., 1978, 1981; Arijs et al., 1980, 1982, 1983b; Henschen and Arnold, 1981; Arnold and Henschen, 1982; Ingels et al., 1985). A total of 106 mixing ratio values are contained within this envelope E. The dotted line F in Figure 2 is obtained by fitting a second degree curve through the 106 data points, so that

$$\log \mu(\text{CH}_3\text{CN}) = A + B.z + C.z^2 \quad (3)$$

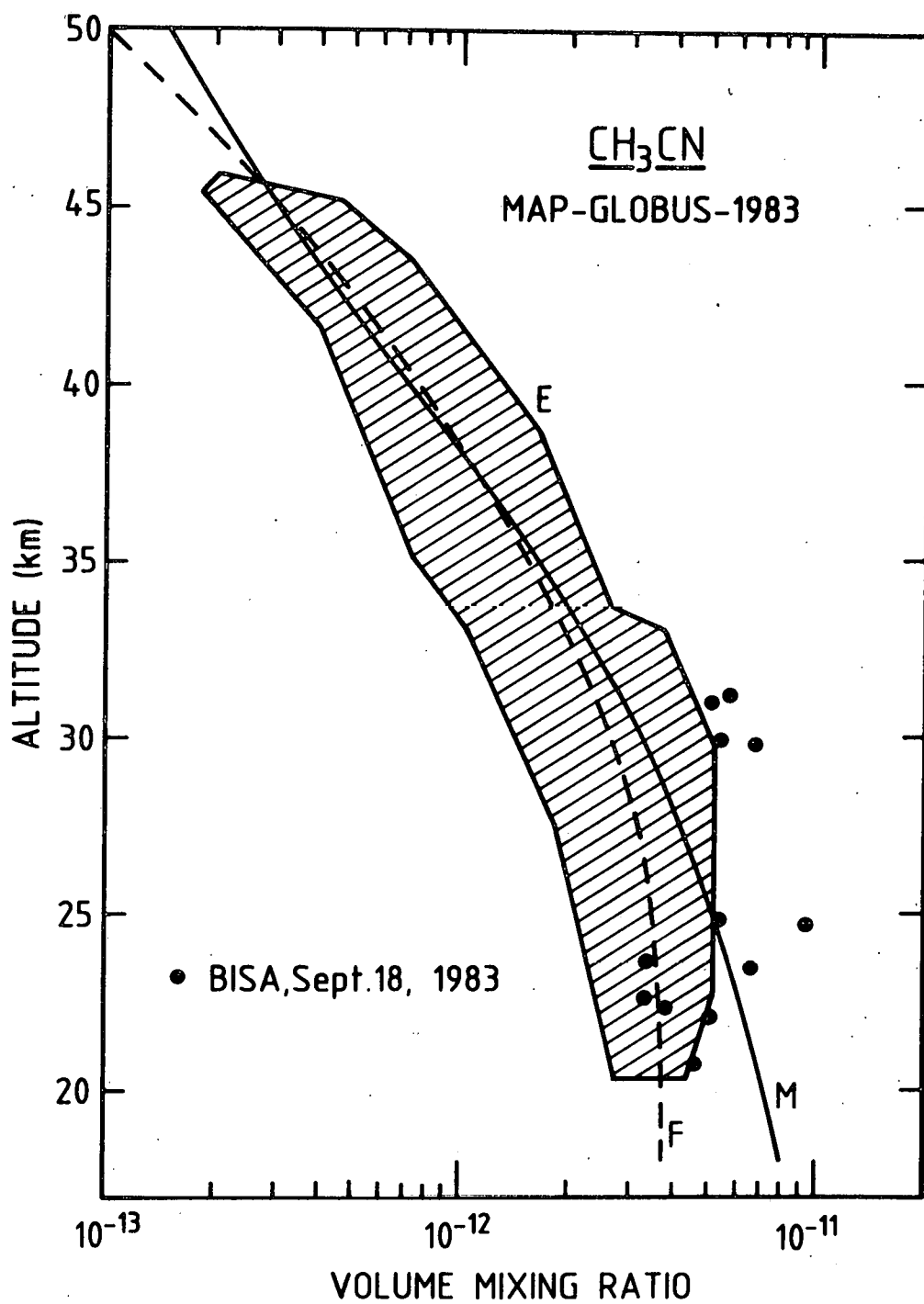


Fig. 2.- Acetonitrile volume mixing ratios as obtained in the MAP Globus 1983 campaign compared to previous measurements (shaded area E) and a model calculation (M). The dotted line F represents a fitting through earlier data points.

Table 2 : Acetonitrile mixing ratios as inferred from positive ion spectra in the S-83 flight.

Altitude (km)	Mixing ratio x 10 <sup>12</sup>
31.2	5.5
31.0	5.0
30.0	5.4
29.8	6.6
25.0	5.2
24.7	9.5
23.7	3.4
23.5	6.8
22.6	3.3
22.4	3.8
22.1	5.0
20.8	4.7

where  $z$  is the altitude in km. It is found that  $A = -28.01$ ,  $B = 0.1678 \text{ km}^{-1}$ , and  $C = -4.127 \times 10^{-3} \text{ km}^{-2}$ . The standard deviation of the logarithm of the data points from curve F is given by  $S = 0.352$  which translates into a factor of 1.42 for the mixing ratio itself. The full line M is the result of a model calculation for  $\text{CH}_3\text{CN}$  (Arijs and Brasseur, 1986), adopting a global surface emission strength of  $4.7 \times 10^{10} \text{ g}$  and assuming that acetonitrile is destroyed mainly by reactions with OH and atomic oxygen. A detailed discussion of this 1-D model is given by Arijs and Brasseur (1985).

As can be seen from Figure 2, the discrepancies between the  $\text{CH}_3\text{CN}$  mixing ratios obtained during our MAP Globus flight and the curves M and F seem to be larger than those observed in previous flights. Most of the points actually fall out of the envelope E of all previous measurements. It is clear therefore that the  $\text{CH}_3\text{CN}$  profile observed in this flight is deviating to a larger extent from an expected mean profile than the earlier data. Similar deviations have been observed in this campaign in the mixing ratio profiles of other trace gases and are discussed to a larger extent in a separate paper by Offermann et al. (this issue).

In order to compare the deviations with those measured during the MAP Globus 1983 campaign derived for other trace gases such as  $\text{O}_3$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{CF}_2\text{Cl}_2$ , we have presented them in the same way, i.e. the quotient of the mixing ratios as derived from the ion mass spectra and those given by a reference profile are shown as a function of altitude in Figure 3. However in making a comparison, some important points need to be kept in mind.

1. The choice of a reference profile for  $\text{CH}_3\text{CN}$  is not straightforward. Curve F (a fit to previous experimental data) is only representative for a limited number of data, all obtained by the same technique and in a limited altitude range (20 to 45 km), where the data above 40 km only result from one balloon flight. In addition, the choice of curve M (a



model calculation) is somewhat arbitrary, since it was shown (Arijs and Brasseur, 1986; Ingels et al., 1986) that different model profiles, agreeing reasonably with experimental results can be obtained, depending upon the use of the  $\text{CH}_3\text{CN}$  emission strength, reaction rates and eddy diffusion coefficients used in the model calculations. We have adopted here a model result giving the best agreement with experimental  $\text{CH}_3\text{CN}$  mixing ratios between 20 and 45 km and resulting in ion distributions consistent with experimentally obtained ones (Ingels et al., 1986).

In view of the difficulty in choosing a so-called reference profile, the deviations from both curves M and F are displayed in Figure 3. Also shown in Figure 3 are the limits for the deviations given by one and two standard deviations from the fitting F, labeled S and 2S respectively.

2. The experimental uncertainties on  $\text{CH}_3\text{CN}$  mixing ratios derived from flight S-83 are estimated to be of the order of 20 to 30% above 25 km and to be somewhat larger below this altitude due to less complete counting statistics in the low altitude spectra. This uncertainty however does not take into account possible errors on the values of  $k_1$ ,  $\alpha$  and  $[n^-]$  used here.

Nevertheless the deviations from the "standard" profiles around 30 km as shown in Figure 3, are larger than those observed for earlier flights and they seem to suggest the presence of a larger disturbance in the stratosphere. Below 25 km, the S-83 data show a considerable amount of scatter and it is difficult to be conclusive about the deviations, especially in view of the dilemma in choosing the exact reference profile (M or F). Disturbances giving rise to temporal variances (or deviations from standard profiles) can be ascribed to dynamics or transport phenomena (Ehhalt et al., 1983). The present set of data on its own however, does not allow to speculate on the nature of the dynamical processes (waves, tides, or other) involved here. A more detailed analysis of all profiles obtained for other trace gases in this MAP Globus

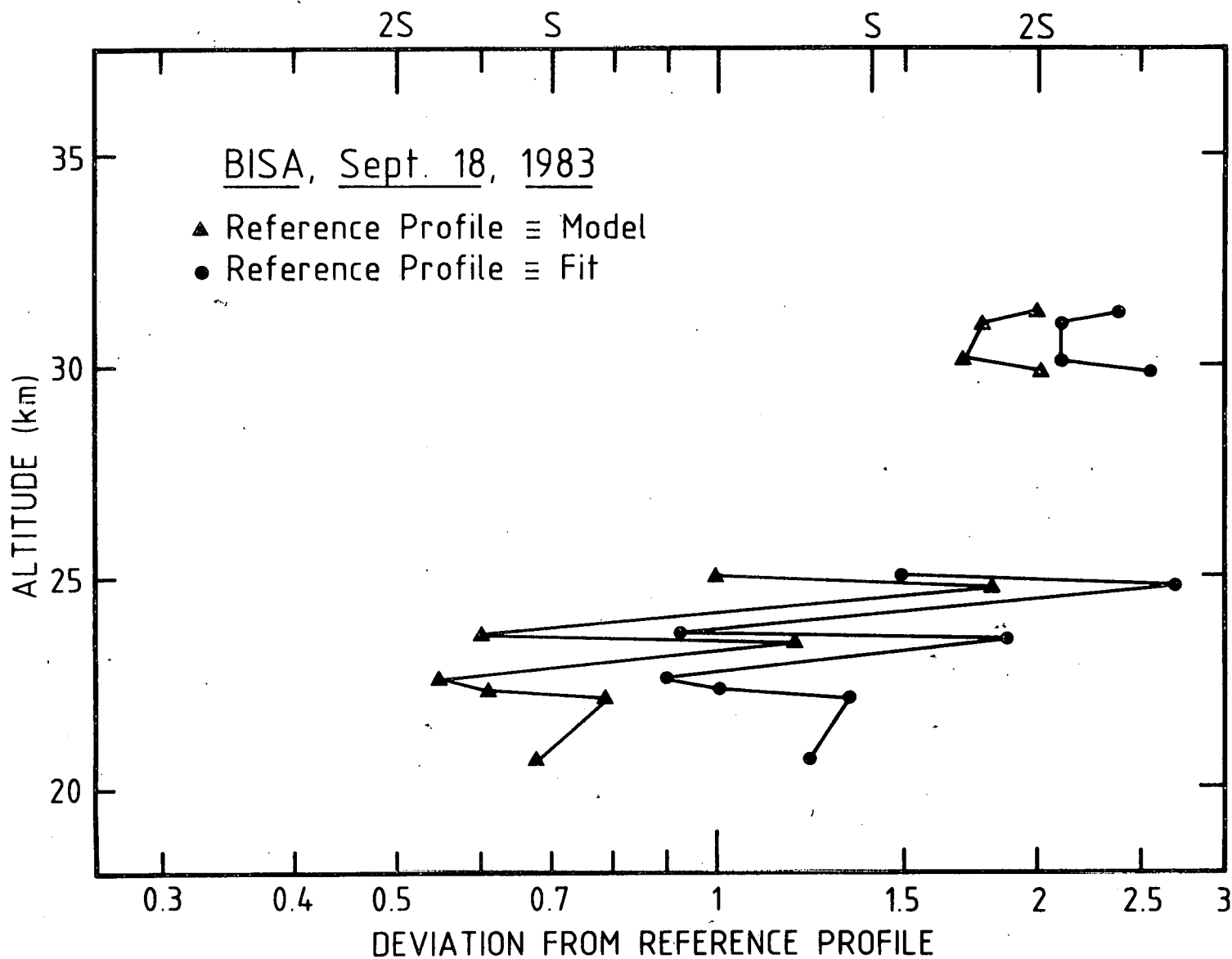


Fig. 3. Deviation of present  $\text{CH}_3\text{CN}$  volume mixing ratios from reference profiles F and M expressed as quotients of the actual data and reference values. S and 2S are one and two standard deviations from the fitting F (for details see text).

1983 campaign is needed to do so. It should be noted however that  $\text{CH}_3\text{CN}$  is a good trace gas to use in such an analysis, in view of the long life time of this molecule (0.5 to 1.4 years; Arijs and Brasseur, 1985).

### 3.2. Negative ions and sulfuric acid concentrations

During a considerable part of the descent from float altitude down to 22 km, measurements were performed in the negative ion mode. Typical spectra as well as a more detailed discussion of the negative ion composition data of flight S-83 have already been given elsewhere (Arijs et al., 1985). The observed major ions were  $\text{NO}_3^-(\text{HNO}_3)_n$  and  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_1(\text{HNO}_3)_m$  clusters, indicated hereafter by  $n_N^-$  and  $n_S^-$  respectively. Due to the fact that conversion of  $n_N^-$  to  $n_S^-$  ions proceeds through a reaction with sulfuric acid vapour



with a reaction rate coefficient  $k_2$  measured in the laboratory (Viggiano et al., 1980, 1982), the spectra allow a derivation of the  $\text{H}_2\text{SO}_4$  number density through the steady state equation

$$k_2 [\text{H}_2\text{SO}_4 + \text{HSO}_y] [n_N^-] = \alpha [n_S^-] [n^+] \quad (4)$$

where square brackets stand for number densities and  $[n^+]$  is the total positive ion density. The term  $\text{HSO}_y$  in equation (4) represents possible other sulfur bearing gases also leading to conversion of  $n_N^-$  to  $n_S^-$  clusters. It has been suggested that these gases mainly consist of  $\text{HSO}_3$  (Arnold et al., 1982), which is an intermediate product in the formation of  $\text{H}_2\text{SO}_4$ , produced by the reaction



Recently however, it was suggested by Stockwell and Calvert (1983) that further conversion of  $\text{HSO}_3$  proceeds through



If however this reaction is the major loss process for  $\text{HSO}_3$ , then the presence of  $\text{HSO}_3$  in measurable quantities in the stratosphere would become very doubtful, as was indicated before (Arijs et al., 1985).

Recent laboratory measurements by Margitan (1984) showed that the rate constant for reaction (6) was  $(4 \pm 2) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ , allowing to conclude that the presence of  $\text{HSO}_3$  in the stratosphere is very unlikely. Therefore we believe that the  $\text{H}_2\text{SO}_4 + \text{HSO}_y$  number density derived from equation (4) mainly consists of  $[\text{H}_2\text{SO}_4]$ .

The  $\text{H}_2\text{SO}_4$  number densities as derived from flight S-83 are shown in Figure 4. The shaded area in this figure corresponds to the envelope of all previous data (Arijs et al., 1982, 1983c, 1983d, 1985; Arnold and Fabian, 1980; Arnold et al., 1981; Arnold and Bührke, 1981; Arnold and Qiu, 1984) the dotted line represents a vapour pressure calculation by a procedure explained elsewhere (Arijs et al., 1983c). Although calculations of the vapour pressure were made assuming a flat surface of a  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  mixture, it can easily be shown that the results will differ only by a few percent using spherical surfaces with a radius of the order of 0.05 to 0.1  $\mu\text{m}$ , i.e. the typical dimensions of stratospheric aerosols.

Taking into account the error bars, the data fall reasonably well within the envelope of the previous results, and no marked deviations due to transport effects, as suggested by the data of  $\text{CH}_3\text{CN}$ , are noticed around 30 km. It is tempting to conclude that the larger supersaturation of the inferred  $\text{H}_2\text{SO}_4$  concentration below about 25 km altitude compared with the mean value of the previous results also reflects interaction of dynamical processes. This conclusion however is rather speculative because of the large uncertainties on the  $\text{H}_2\text{SO}_4$  concentrations due to the low count rate observed in the negative ion spectra obtained below 25 km. It should also be kept in mind however that most of the earlier data

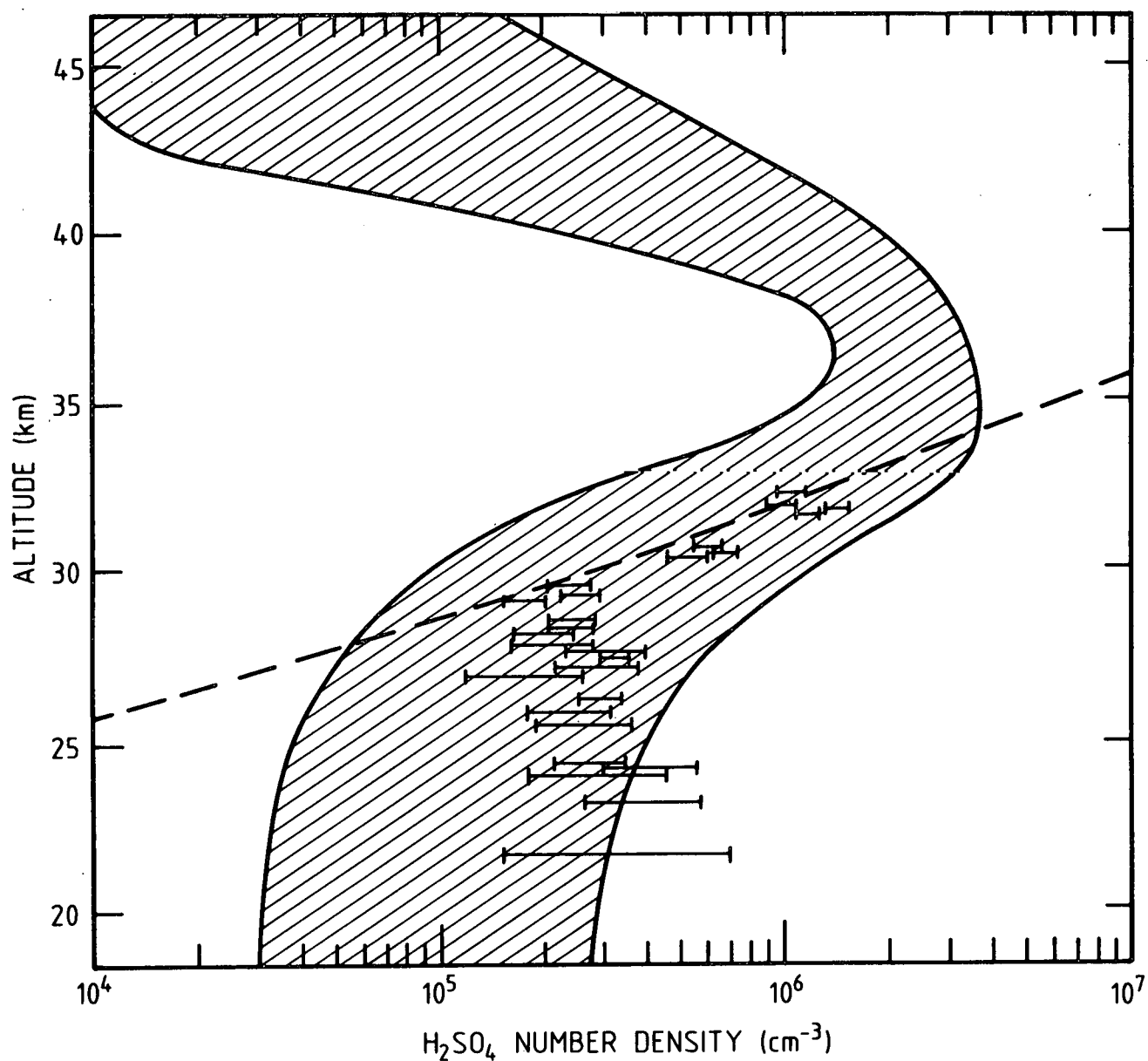


Fig. 4.- Sulfuric acid concentrations derived from negative ion composition data obtained in the MAP Globus 1983 campaign compared to earlier data (shaded area) and a vapour pressure calculation (dotted line). Error bars are due to uncertainties in ion abundance measurements and not to uncertainties in kinetic data.

about  $\text{H}_2\text{SO}_4$  were obtained during the period from June until October 1982 after the eruption of the volcano El Chichon (4 April 1982). This eruption resulted in a disturbed stratospheric sulfur chemistry due to injections of large supplementary quantities of  $\text{SO}_2$  and other sulfur bearing gases. It is therefore very difficult to derive an average  $\text{H}_2\text{SO}_4$  profile from the previous data and an analysis similar to the one for  $\text{CH}_3\text{CN}$  would probably not be representative.

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