

Stratospheric aerosol sulfuric acid: First direct in situ measurements using a novel balloon-based mass spectrometer apparatus

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Abstract. The first direct in situ measurements of the sulfuric acid contained in stratospheric aerosol particles were made using a novel balloon-based Ion Molecule Reaction Mass Spectrometer instrument (IMRMS) equipped with an aerosol vaporizer. The IMRMS method employed offers direct aerosol sulfuric acid measurements with high spatial resolution. The balloon flight took place on 23 October 1995 in middle latitudes (44°N) and reached a maximum altitude of 24 km. Measured molecular number densities of aerosol sulfuric acid decreased with increasing altitude from about $2.9 \times 10^9 \text{ cm}^{-3}$ at 15 km altitude to about $2.4 \times 10^8 \text{ cm}^{-3}$ at 21 km. Corresponding mass mixing ratios are 2.5 and 0.6 ppbm, respectively. Calculated sulfuric acid mixing ratios from aerosol volumes inferred from aerosol size distribution measurements on the same balloon agree well with the IMRMS data using standard assumption aerosol composition.

Key words: Stratospheric aerosol, sulfuric acid, mass spectrometry

1. Introduction

Stratospheric aerosol particles influence ozone and at least temporarily also climate and therefore are of considerable current interest (Turco et al., 1982) (Fahey et al., 1993) (WMO, 1995). These particles have typical measured radii between 0.05 and 0.15 μm and are thought to be mostly composed of sulfuric acid (H_2SO_4 hereafter SA) and water. Indications for SA come from stratospheric sampling experiments using chemical filters which were analyzed in the laboratory at the ground after return from balloon or high altitude aircraft flights (Sedlacek et al., 1983) (Lazrus et al., 1974). Usually sulfate was detected which suggests that the droplets contain SA. Another strong indication for SA containing droplets comes from measurements of gaseous SA (GSA) in the stratosphere which were originally made by our group (Arnold and Fabian, 1980) (Arnold and Bührke, 1983) (Krieger and Arnold, 1994). These GSA measurements suggest that at altitudes between about 30 and 35 km GSA is in equilibrium with the droplets. If so, the measured GSA partial pressure represents the equilibrium saturation SA vapor pressure of the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ aerosols (hereafter SAWA). Indeed the measured GSA pressure is close to the expected GSA equilibrium pressure. The formation of stratospheric SAWA is thought to proceed mostly by heterogeneous

SAW condensation involving pre-existing nuclei which become transported into the stratosphere from below and above (Turco et al., 1982). Nuclei of tropospheric origin may to some part also be composed of SAW, possibly formed in the upper tropical troposphere via homogeneous SAW nucleation (Brock et al., 1995). Nuclei of upper atmospheric origin may be preferably "meteor smoke" particles formed by recondensation in meteor tails (Schulte and Arnold, 1992)(Hunten et al., 1980). Stratospheric GSA is thought to be formed in the stratosphere via photooxidation of SO_2 which may originate from photooxidation of reduced sulfur gases particularly CSO (Crutzen, 1976) or episodic direct injections by volcanic eruptions (McKeen et al., 1984) (Bluth et al. 1992) (Arnold et al., 1990). The present paper reports on the first direct in situ detection and quantitative measurement of aerosol SA in the stratosphere along with measurements of the aerosol size distribution.

2. Measurements

The aerosol SA measurements were made by a balloon-based IMRMS equipped with a vaporizer. This instrument which hereafter will be termed VACA (Volatile Aerosol Composition Analyzer) was developed and built by MPIK Heidelberg. A detailed description of the IMRMS method and its balloon-based application can be found in (Arnold and Knop, 1987)(Möhler and Arnold, 1991). For the additional new features of the VACA method a first description will be given here. A more detailed description can be found in (Curtius et al., 1997). A schematic representation of the apparatus is shown in figure 1. Atmospheric air is passed through the vaporizer and the flow reactor by the action of an air fan. The air is heated to a temperature around 200°C leading to evaporation of SAWA. The vaporizer consists of a manifold of heated copper cylinders. The small cylinders in the manifold ensure sufficient heat transfer from the metal to the flowing air. The air temperature is measured with several sensors along the flow path. Downstream of the vaporizer the air, now containing GSA liberated by the evaporation of SAWA, is passed through a flow tube into which reactant ions of the type $\text{NO}_3^- (\text{HNO}_3)_n$ ($n = 0, 1, 2$) are introduced. The latter react with GSA via ion molecule reactions of the type



which have been originally proposed by Arnold and Fabian (1980) and which nearly occur on every collision to produce $\text{HSO}_4^- (\text{HNO}_3)_n$. Measured rate coefficients k_n are 2.6, 2.3, and 1.1 in units of $10^{-9} \text{cm}^3 \text{s}^{-1}$ for $n = 0, 1,$ and 2 , respectively (Viggiano et al., 1982). Downstream of the flow tube reactant and product ions are measured by a cryogenically (liquid neon) pumped quadrupole mass spectrometer. The time span τ the ions reside in the flow tube

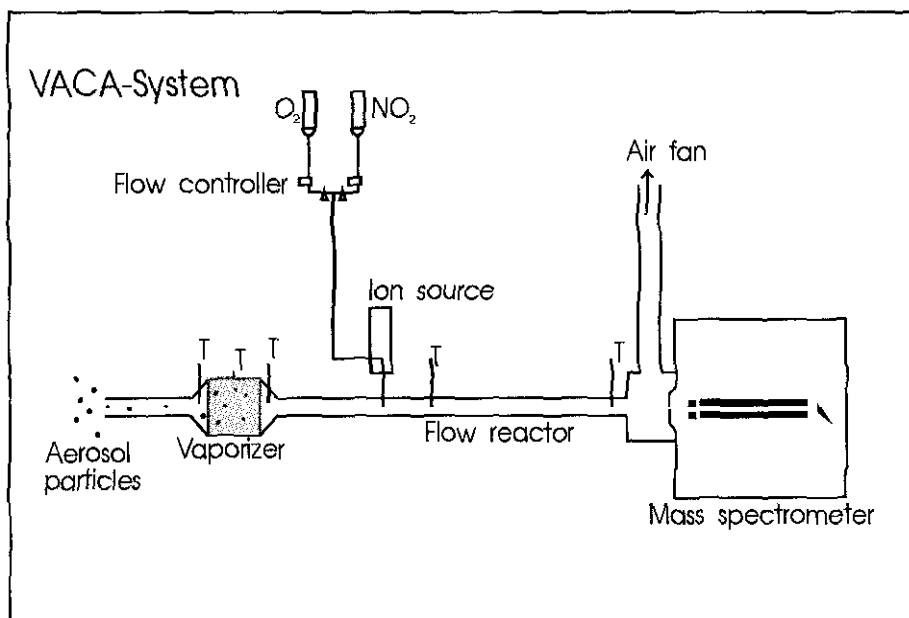


Figure 1. Schematics of the Volatile Aerosol Composition Analyzer system (VACA). Along with the ambient air aerosol particles are drawn into the flow tube system (4 cm diameter, stainless steel sampling line, with a typical flow velocity of 15 m/s). The volatile compounds of the particles are evaporated at temperatures around 200°C in the vaporizer. The gaseous sulfuric acid is detected using ion molecule reaction mass spectrometry (IMRMS).

is measured and the GSA concentration in the flow tube can be determined using the expression $[H_2SO_4] = \ln(R + 1) / (k\tau)$ where k is the effective rate coefficient for (1) and R is the ratio of product and reactant ions. For $k = 2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, $\tau = 0.05 \text{ s}$, and $R \geq 0.01$ the GSA detection limit becomes $1 \times 10^8 \text{ cm}^{-3}$. In comparison the maximum concentration of ambient stratospheric GSA is at most only about $3 \times 10^6 \text{ cm}^{-3}$ (c. f. (Arnold, 1992)). The mass spectrometer instrument used during the balloon flight reported here yields a precision of about $\pm 40\text{--}50\%$, caused mostly by the statistical error of the mass spectroscopic data and by errors due to overlap of neighboring mass peaks. The total accuracy amounts to about $\pm 65\%$, due to the uncertainty of the rate coefficient of $\pm 50\%$. Note that k does not depend on pressure and therefore the relative shape of the profile is not influenced by the accuracy of k . Since the temperature of the whole flow reactor was above 100°C during the measurement the error caused by wall losses is negligible.

The balloon measurements reported here, performed within the framework of SESAME (Second European Stratospheric Arctic and Mid-latitude Experiment), took place on 23 October 1995 over southern France (44°N). During the balloon ascent to 24 km the vaporizer, flow tube and IMRMS remained

vacuum sealed to avoid any in-flight contamination of the thoroughly baked out system. Only at the beginning of the valve-controlled balloon descent ($v_{\text{des}} \approx 1.1$ m/s) the instrument was opened and aerosol SA measurements started. Measurements continued to a lowest height of 14 km.

Measurements of the aerosol number concentration at several sizes were made by an Optical Particle Counter (OPC) and a Condensation Nuclei Counter (CNC) of the University of Wyoming during the same balloon flight. The total error of the aerosol volume inferred from aerosol size distributions fitted to the aerosol concentration measured is estimated to be 30 % (Deshler et al., 1993).

3. Results and Discussion

Figure 2 shows the vertical distribution of measured total GSA number densities (aerosol SA and ambient GSA). The concentration decreases from $2.9 \times 10^9 \text{cm}^{-3}$ (15 km) to $2.4 \times 10^8 \text{cm}^{-3}$ (21 km) and is always much larger than previously measured ambient GSA ($\leq 3 \times 10^6 \text{cm}^{-3}$). Hence, the measured total GSA must be mostly due to vaporized aerosol SA. The H_2SO_4 number densities inferred from aerosol concentration measurements with OPC and CNC are also shown. Size distributions fitted to the concentration were used to calculate the total aerosol volume. The sulfuric acid number density was then inferred by assuming spherical droplets with an H_2O mass fraction in equilibrium with ambient atmospheric water vapor (Turco et al., 1982). A mean aerosol acid weight percentage of 70% H_2SO_4 and 30% H_2O was assumed, which is expected at 45°N at altitudes between 15 and 21 km in October according to Yue et al. (1994). The number densities measured by VACA agree well with the densities determined from the aerosol size distributions (descent) except for 15 to 15.5 km. The differences around 15 km altitude are possibly caused by the low sensitivity of the spectrometer at this altitude due to the high gas pressure which raised the precision to more than 50 %. The descent data of the OPC at altitudes below 15 km seems to be influenced by debris from ballast releases.

Vertical profiles of sulfuric acid mass mixing ratio carried in aerosols from are shown in figure 3 from October 1995 and from previously obtained data. The profile of 15 November 1993 inferred from aerosol measurements at Laramie (41°N) refers to a volcanically perturbed situation (29 months after the eruption of Mount Pinatubo). By the time of our balloon flight of 23 October 1995 most of the volcanic SAWA had left the stratosphere. The October 1995 profile is about seven times lower than the November 1993 profile which corresponds to an $1/e$ lifetime of stratospheric SAWA of about 12 months. This inferred lifetime is in close agreement with previous estimations (c. f. (WMO, 1995)). Figure 3 also shows previous data obtained by

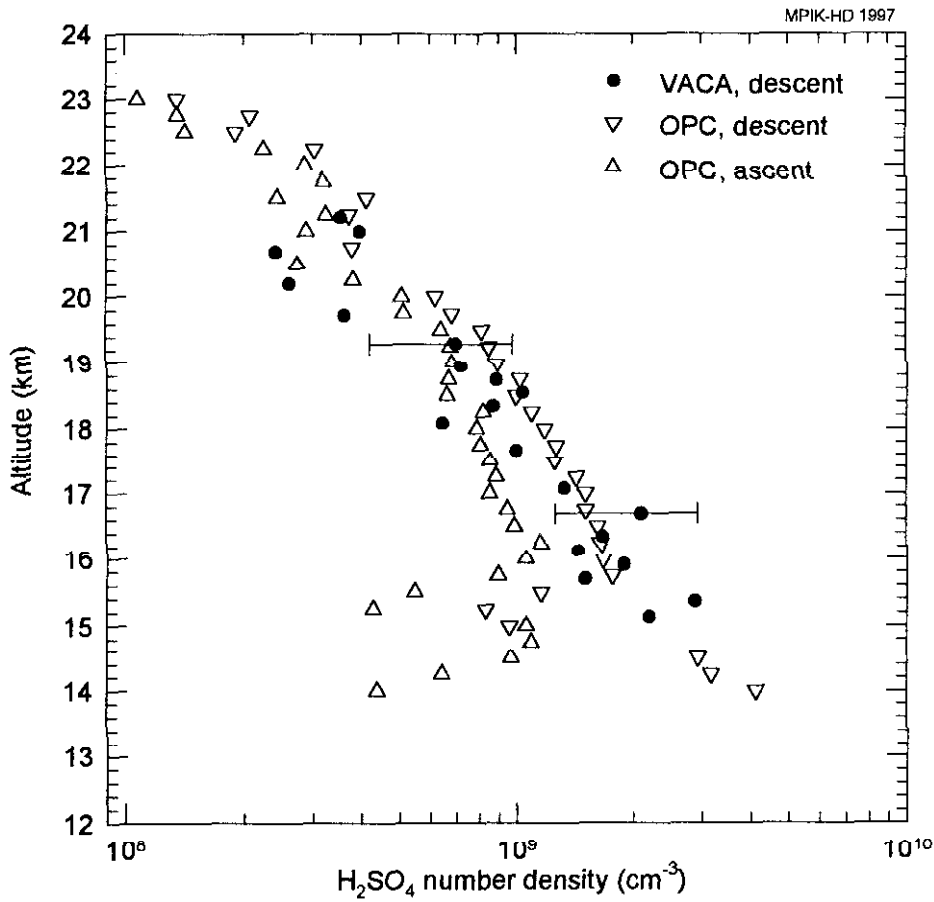


Figure 2. Total sulfuric acid number densities measured on 23 October 1995 around 44°N , 0.5°E during descent by the balloon-based Volatile Aerosol Composition Analyzer (VACA) (●). Aerosol sulfuric acid inferred from measurements of aerosol number distributions on ascent (Δ) and descent (∇) by the optical particle counter (OPC).

collecting stratospheric aerosols on chemical filters with subsequent analysis in the laboratory (Sedlacek et al., 1983). The summer 1973 profile refers to a volcanically unperturbed situation while the May 1975 profile refers to a situation disturbed by the eruption of the volcano Mount Fuego. These profiles are shown to give an impression of the typical range of aerosol sulfuric acid to be expected in the stratosphere in situations not heavily disturbed by major volcanic eruptions.

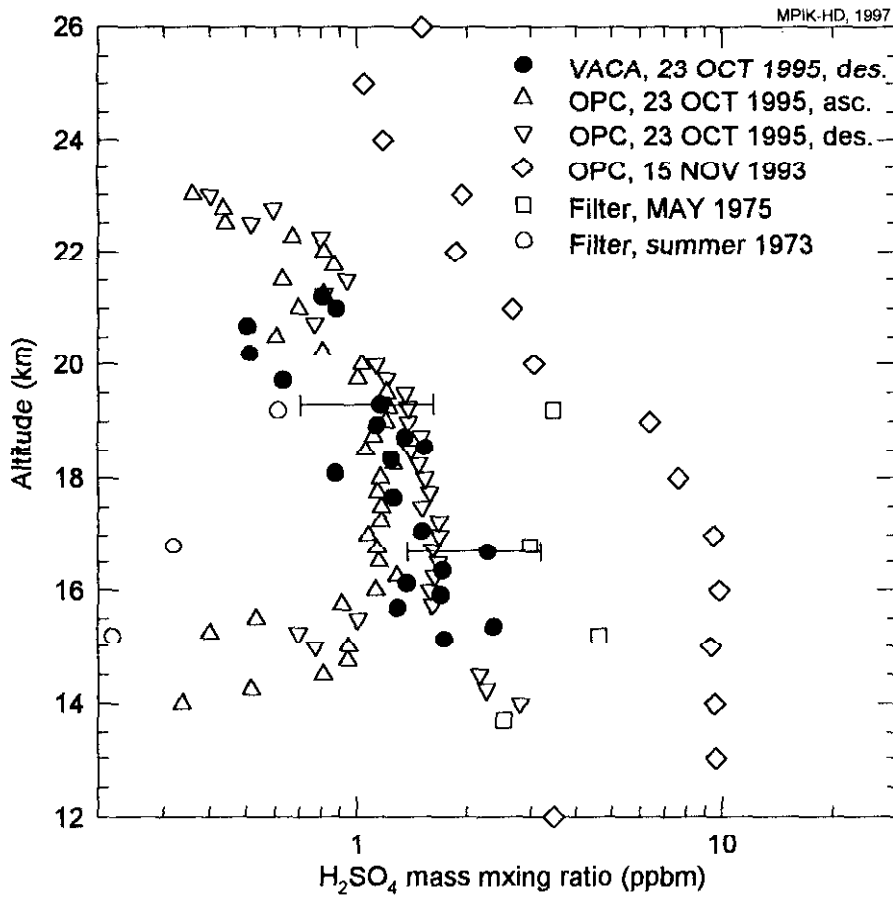


Figure 3. Aerosol sulfuric acid mass mixing ratios inferred from VACA measurements (\bullet), from OPC data (Δ , ∇ : 23 Oct 1995, ascent and descent; \diamond : 15 Nov. 1993 about $2\frac{1}{2}$ year after the eruption of Mount Pinatubo) and for comparison results from sampling experiments using chemical filters with subsequent laboratory analysis of stratospheric aerosol during summer 1973 (\circ) and May 1975 (\square) (Sedláček et al., 1983).

4. Summary and Conclusions

The first direct in situ measurements of stratospheric aerosol sulfuric acid were made using a novel balloon-based mass spectrometer apparatus (Volatile Aerosol Composition Analyzer VACA). Our results confirm the common assumption that global stratospheric aerosols are in fact composed mostly of sulfuric acid. Measured molecular number densities for aerosol SA decrease from about $2.9 \times 10^9 \text{ cm}^{-3}$ (15 km) to about $2.4 \times 10^8 \text{ cm}^{-3}$ (21 km). Corresponding mass mixing ratios are 2 ppbm and 0.6 ppbm, respectively. In the

near future we plan to carry out direct aircraft-based high spatial resolution measurements of aerosol sulfuric acid in the lower stratosphere and upper troposphere.

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References

- Arnold, F., and K. Fabian, First measurements of gasphase sulfuric acid in the stratosphere, *Nature*, **283**, 55–57, 1980.
- Arnold, F. and Th. Bührke, New H₂SO₄ and HSO₃ vapour measurements in the stratosphere - evidence for a volcanic influence. *Nature*, **301**, 293–295, 1983.
- Arnold, F. and G. Knop, Stratospheric trace gas measurements using a new balloon-borne ACIMS method, *Int. J. of Mass Spectrometry and Ion Processes*, **81**, 33–44, 1987.
- Arnold, F., Th. Bührke, and S. Qiu, Evidence for stratospheric ozone-depleting heterogeneous chemistry on volcanic aerosols from El Chichón, *Nature*, **348**, 49–50, 1990.
- Arnold, F., Stratospheric aerosol increases and ozone destruction: Implications from mass spectrometer measurements, *Berichte der Bunsengesellschaft für Physikalische Chemie*, **96**, 339–350, 1992.
- Bluth, G. J. S., S. D. Doiron, C. C. Schnetzler, A. J. Krueger, L. S. Walter, Global tracing of the SO₂ clouds from June 1991 Mount Pinatubo eruptions, *Geophys. Res. Lett.*, **19**, 1992.
- Brock, C. A., P. Hamill, J. C. Wilson, H. H. Jonsson, K. R. Chan, Particle formation in the upper tropical troposphere: A source of nuclei for the stratospheric aerosol, *Science*, **270**, 1995.
- Crutzen, P. J., The possible importance of CSO for the sulfate layer in the stratosphere, *Geophys. Res. Lett.*, **3**, 73–76, 1976.
- Curtius, J., S. Spreng, and F. Arnold, A novel balloon-based mass spectrometer apparatus for direct in situ aerosol composition analyses: Experimental setup, laboratory measurements and first results, *in preparation*.
- Deshler, T., B. I. Johnson, and W. R. Rozier, Balloonborne measurements of Pinatubo aerosol during 1991 and 1992 at 41°N, vertical profiles, size distribution, and volatility, *Geophys. Res. Lett.*, **20**, 1435–1438, 1993.
- Fahey, D. W., S. R. Kawa, E. L. Woodbridge, P. Tin, J. C. Wilson, H. H. Johnson, J. E. Dye, D. Baumgardner, S. Borrmann, D. W. Tooney, L. M. Avallone, M. H. Proffit, J. Margitan, M. Loewenstein, J. R. Podolske, R. J. Salawitch, S. C. Wofsy, M. K. M. Ko, D. E. Anderson, M. R. Schoeberl, and K. R. Chan, In situ measurements constraining the role of sulphate aerosols in mid-latitude ozone depletion. *Nature*, **363**, 509–514, 1993.
- Huntten, D.M., R.P. Turco and O.B. Toon, Smoke and Dust Particles of Meteoric Origin in the Mesosphere and Stratosphere, *J. Atmos. Sci.*, **37**, 1342–1357, 1980.

- Krieger, A. and F. Arnold, First composition measurements of stratospheric negative ions and inferred gaseous sulfuric acid in the winter arctic vortex – implications for aerosols and hydroxyl radical formation, *Geophys. Res. Lett.*, **21** (EASOE special issue), 1259–1262, 1994.
- Lazrus, A. L., B. W. Gandrud, Stratospheric sulfate aerosol, *J. of Geophys. Res.*, **79**, 3424–3431, 1974.
- McKeen, S. A., S. C. Liu, C. S. Kiang, On the chemistry of stratospheric SO₂ from volcanic eruptions, *J. of Geophys. Res.*, **89**, D3, 4873–4881, 1984.
- Möhler, O., and F. Arnold, Flow reactor and triple quadrupole mass spectrometer investigations of negative ion reactions involving HNO₃: Implications for atmospheric HNO₃ detection by chemical ionization mass spectrometry, *J. of Atmospheric Chem.*, **13**, 33–61, 1991.
- Schulte, P., and F. Arnold, Detection of upper atmospheric negatively charged microclusters by a rocket-borne mass spectrometer, *Geophys. Res. Lett.*, **19**, No. 23, 2297–2300, 1992.
- Sedlacek, W., A., E. J. Mroz, A. L. Lazrus, and B. W. Gandrud, A decade of stratospheric sulfate measurements compared with observations of volcanic eruptions, *J. of Geophys. Res.*, **88**, 3741–3776, 1983.
- Turco, R. P., R. C. Whitten, and O. B. Toon, Stratospheric aerosols: Observation and theory, *Rev. of Geophysics and Space Physics*, **20**, No. 2, 233–279, 1982.
- Viggiano, A. A., R. A. Perry, D. L. Albritton, E. E. Ferguson, and F. C. Fehsenfeld, Stratospheric negative-ion reaction rates with H₂SO₄, *J. of Geophys. Res.*, **87**, 7340–7342, 1982.
- World Meteorological Organisation (WMO), Scientific Assessment of Ozone Depletion 1994, WMO global ozone research and monitoring project – Report No. 37, 1995.
- Yue, G., K., L. R. Poole, P. H. Wang, E. W. Chiou, Stratospheric aerosol acidity, density, and refractive index deduced from SAGE II and NMC temperature data, *J. of Geophys. Res.*, **99**, 3727–3738, 1994.