First direct sulfuric acid detection in the exhaust plume of a jet aircraft in flight

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Abstract. Sulfuric acid (SA) was for the first time directly detected in the exhaust plume of a jet aircraft in flight. The measurements were made by a novel aircraft-based VACA (Volatile Aerosol Component Analyzer) instrument of MPI-K Heidelberg while the research aircraft Falcon was chasing another research aircraft ATTAS. The VACA measures the total SA in the gas and in volatile submicron aerosol particles. During the chase the engines of the ATTAS alternatively burned sulfur-poor and sulfur-rich fuel. In the sulfur-rich plume very marked enhancements of total SA were observed of up to 1300 pptv which were closely correlated with ΔCO_2 and ΔT and were far above the local ambient atmospheric background-level of typically 15-50 pptv. Our observations indicate a lower limit for the efficiency ε for fuel-sulfur conversion to SA of 0.34 %.

Introduction

Sulfuric acid (SA) is thought to be formed in the exhaust plumes of jet aircraft and to have potentially important roles including new aerosol particle (AP)-formation, soot-activation, and eventually even water-contrail formation (cf. *Friedl*, 1997). The influence of SA depends critically on the rate of SA-formation which in turn is determined by fuel consumption, the fuel-sulfur content (FSC) and the efficiency ε of fuel-sulfur conversion to SA. The great interest in aircraft produced SA and its effects has stimulated numerous modeling activities as well as experimental work. In particular laboratory-investigations of gaseous SA (GSA)-formation indicate that SO_3-conversion to GSA is fast enough to ensure rapid GSA-formation in the exhaust plume of an aircraft (*Reiner and Arnold*, 1993). This was further supported by additional laboratory measurements which confirmed the above findings but in addition also investigated the temperature-dependence of the SO_3-conversion (*Kolb et al.*, 1994; *Lovejoy et al.*, 1996). A series of flight experiments showed that variations in the fuel sulfur content between 2 and 5500 ppmm cause changes in the properties of fresh aircraft exhaust plumes (*Schumann et al.*, 1996; *Petzold et al.* 1997, *Busen and Schumann*, 1995).

However despite the great interest in aircraft produced SA this molecule has so far not been directly detected in the exhaust plume of a jet aircraft in flight. Recent ground-level measurements of chemiions in jet fuel combustion (*Frenzel and Arnold*, 1994) succeeded in detecting GSA. More recently both GSA and

its precursor SO_3 were measured in the exhaust of the research aircraft ATTAS at the ground (*Arnold et al.*, 1997a) and the ratio $[SO_3+GSA]/[\text{total sulfur}]$ was found to be around 1.2 %. A search (*Arnold et al.*, manuscript submitted to GRL, 1998) for GSA in the exhaust plume of an Airbus in flight revealed the virtual absence of GSA. Only an upper limit of 5×10^7 per cm^3 was obtained which was much smaller than the expected total SA. This finding was interpreted in terms of rapid gas-to-particle-conversion of GSA leading to sulfuric acid-water aerosol particles (SAW-APs) or SAW-coated soot. Recently an efficiency of 0.5 % for the fuel-sulfur conversion to GSA via OH was estimated from HONO and HNO_3, measured in a jet aircraft plume (*Tremmel et al.*, 1997).

From aerosol volatility measurements in the wake of the supersonic Concorde aircraft which took place at much larger plume ages (13-58 minutes) and with a different engine than the above measurements, ε-values of 12-45 % were indirectly inferred (*Fahey et al.*, 1996). However the chemical nature of the volatile APs was not measured but assumed to be a sulfuric acid-water (SAW) solution with an equilibrium composition (SA-mass fraction about 70 %). This assumption was supported by the fact that the temperature at which the particles evaporated was consistent with SAW-APs.

Modeling studies assuming all fuel sulfur to be emitted as SO_2 at the exit plane of the engine indicate conversion efficiencies via gas-phase oxidation of SO_2 by OH in the plume of 0.5-2 % (*Kärcher et al.*, 1996, *Brown et al.*, 1996a). Recent predictions of ε using a numerical model which includes the oxidation of fuel sulfur to S(VI) ($SO_3 + H_2SO_4$) inside the engine range from 2 to 6 % for the ATTAS engine and up to 10 % for the Concorde engine (*Brown et al.*, 1996b). According to these results an efficiency of about 2 % for the ATTAS burning fuel with 2700 ppmm S and around 5.5 % for 22 ppmm S is expected. Model calculations by *Kärcher and Fahey*, 1997, can reproduce the aerosol measurements of the Concorde plume when assuming the oxidation of fuel sulfur to SO_3 inside the engine to reach values larger than 20 % which results in ε values of 16-36 %, whereas *Yu and Turco*, 1997, can reproduce the same measurements assuming an ε of 30 % and including the role of ions in aerosol formation and evolution.

Experimental

The present SA-measurements were made by a novel aircraft-based VACA-instrument (VACA = Volatile Aerosol Component Analyzer) which was developed, built and operated by MPI-K Heidelberg and which flew on board of the research aircraft Falcon. Basically this instrument is similar to a balloon based VACA
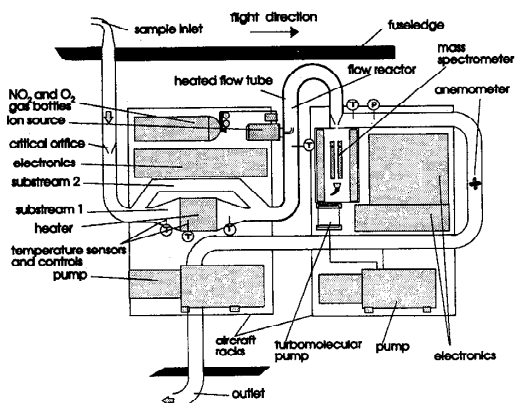
Figure 1. Schematic representation of the aircraft-based VACA instrument (cf. text).

of MPI-K Heidelberg which recently made aerosol-SA measurements in the stratosphere (*Arnold et al.*, 1997b). The VACA measures total SA, which is the sum of gaseous SA and condensed phase SA contained in aerosol particles. The aircraft-based VACA differs from the balloon-based instrument in a few respects. The aircraft-VACA (figure 1) uses a pumped air intake which is facing opposite to the flight direction. Hence only aerosol particles (APs) with sufficiently small sizes are sampled. Larger APs are not sucked into the air intake due to their larger inertia which does not allow them to follow gas stream lines. The backward facing inlet was chosen to avoid anisokinetic sampling of large aerosol particles which would lead to a substantial and poorly defined oversampling of SA contained in contrail water ice particles. We estimate the cutoff size of our inlet similar to the cutoff size determined by *Schröder and Ström*, 1997, to be smaller than 1 µm.

After passing a critical orifice of 2.5 mm diameter the gas stream is split into two equally strong substreams 1 and 2. Substream 1 flows through a heater and thereby the gas temperature is raised to about 190°C. The heater is a copper cylinder with a length of 20 cm and 104 channels each having an inner diameter of 0.4 cm. Note that due to the slow gas flow in the heater (compared to the balloon experiment mentioned above) GSA produced by evaporation of SAW-APs in the heater does not leave the heater due to thermal decomposition of GSA and reactions of GSA at the walls of the narrow heater-channels. This has been demonstrated in laboratory experiments using small artificially generated SAW-APs with slow flow conditions (1-4 m/s).

Downstream of the heater the hot substream 1 merges again with the cool substream 2 (probe-gas stream) which still contains SAW-APs. Thereby the probe-gas is heated to a temperature of 117°C which is the typical temperature measured 30 cm behind the merging point. This results in evaporation of SAW-APs in the merged gas stream avoiding substantial wall losses of SA. Pronounced cooling of the probe gas flow is inhibited by heating the stainless-steel flow tube walls to 100°C-120°C. Thereby wall-losses of GSA due to SAW-condensation at the inner wall of the flow tube are avoided.

At a distance of 35 cm downstream of the merging point reagent-ions of the type NO_3^- (HNO_3)$_m$ are introduced into the flow tube. These ions are produced in a separate little flow reactor by an electrical discharge burning in a gas mixture of O_2, N_2, and NO_2, which also contains some HNO_3. The injected ions may react with GSA (*Arnold and Fabian*, 1980), leading to product ions

of the type HSO_4^- (HNO_3)$_m$ and eventually even HSO_4^- H_2SO_4(HNO_3)$_m$, with rate coefficient k=2.3 × 10^{-9} cm^3/s for m=1 (*Viggiano et al.*, 1982). During the experiment the total gas pressure and gas flow velocity in the ion reaction zone are around 100 hPa and 4 m/s respectively, the diameter of the flow tubes is 4 cm, the reaction zone has a length of 40 cm. At the rear end of the reaction zone ions from the core of the gas stream enter, via an orifice (diameter 0.15 mm), a cryogenically pumped quadrupole mass spectrometer. From the measured abundance ratio R of product-and reagent-ion families with NO_3^- and HSO_4^- cores the GSA-concentration in the ion reaction zone can be determined using the expression [GSA] = ln(1+R) / (k t). For a smallest measurable R=0.0002 one obtains a SA-detection limit of about 1×10^7 cm^{-3}. The uncertainty and precision of the measured SA concentration are ±40 % and ±20 % respectively. The sampling rate is 0.3 Hz.

Several processes may induce SA losses in our experiment and therefore allow only to obtain a lower limit for the SA concentration: Diffusional losses especially of very small aerosol particles (<10 nm) and gaseous SA at the air inlet, sampling losses of large aerosol particles due to the backward facing inlet, losses of GSA and APs at the walls of the tubing and the critical orifice, incomplete evaporation of SAW-APs and the possibility that SA adsorbed on soot particles might not evaporate at the temperatures used. Therefore all measured SA concentrations are considered to be lower limits. Only to correct for the losses of SA occurring in the copper heating device of substream 1 a correction factor of two was applied, which was verified by laboratory measurements.

The ΔCO_2 data (exhaust CO_2 above atmospheric background CO_2) was obtained using a nondispersive infrared CO_2 sensor of DLR-IPA (*Schulte et al.*, 1997). The instrument's range for ΔCO_2 is 250 ppmv. For measurements in the young plume with CO_2 mixing ratio possibly exceeding this range, the sample was diluted at 1:1 mixing ratio under mass flow control with a reference gas containing 360 ppmv of CO_2, extending the range of ΔCO_2 up to 500 ppmv. Measurements of the temperature difference ΔT inside the plume above the atmospheric ambient temperature and the distance d between the two aircraft were provided by DLR-IPA with sensors and GPS methods as in *Petzold et al.*, 1997. ΔT, d, and CO_2 were measured with sampling rates of 1 Hz.

The measurements to be reported took place on 18 April 1997 over Germany at two altitude-levels (8000 m and 9500 m) (*Petzold et al.*, 1997). During the chase both jet-engines (type: Rolls-Royce/SNCEMA M45H Mk501 turbofan engines) of the ATTAS were alternatively burning either sulfur-poor or sulfur-rich fuel with sulfur contents of 22 ± 5 and 2700 ± 300 ppmm. A visible water-contrail was present only at the upper altitude-level (9500 m). The sulfur-rich plume was penetrated during 4 periods of time, each having a length of about 10 minutes. The total range of distances d between the ATTAS and the Falcon covered during these periods was 100-3100 m corresponding to plume ages t_p of about 0.7-20.7 s.

Prior to this "measurement" flight (18 April 1997) an "SA-injection" flight (16 April 1997) was performed during which a liquid mixture of SA and water (38 % SA mass fraction) was injected through stainless steel injection pipes with 4 mm internal diameter at a rate of 0.161 g H_2SO_4 s^{-1} per engine (fuel flow: 164 g s^{-1} per engine for the lower flight level and 151 g s^{-1} per engine for the upper flight level) directly into the centers of the hot exhaust jets (620 K) of the ATTAS at the exit planes of both engines. Heat transfer from the hot exhaust jet to the injection pipe and the large speed (420 m/s) of the exhaust relative to the pipe cause immediate nebulization and partial evaporation of the in-
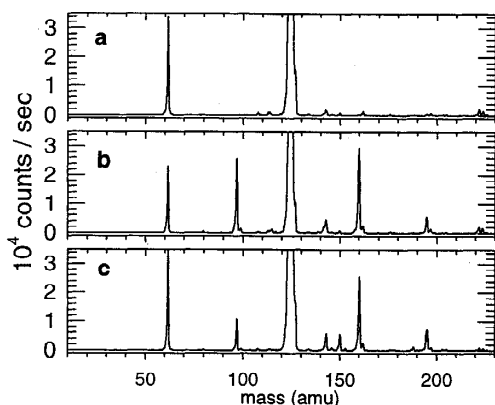
Figure 2. Mass spectra of negative ions obtained by VACA (a) outside the plume (background, 18 April 1997), and (b) inside the exhaust plume (FSC = 2700 ppmm, 18 April 1997) of the ATTAS, and (c) with SAW-AP injection (16 April 1997). Maximum level of m125 ($\approx 1 \times 10^6$ s^{-1}) out of displayed range.

jected SAW. The objective of that flight was to verify the detection of SA contained in APs by the VACA-instrument under flight- and plume-conditions. A quantitative calibration of the sensitivity of SA detection by the VACA instrument can not be achieved by the "SA-injection" flight due to the probable formation of large SA droplets which can not be sampled by the backward facing inlet of the VACA and because some of the injected SA may thermally decompose in the hot exhaust jet. Nevertheless some fraction of the SA was contained in small SAW-APs which offered a convincing qualitative verification of the SA-signatures in the mass-spectra of the VACA operating under flight-conditions.

Results and Discussion

Mass spectra of negative ions obtained by VACA outside and inside the sulfur-rich exhaust plume of the ATTAS at 8 km altitude are shown in figures 2 a, b, and c. Spectrum 2a (outside the

plume) contains mostly reagent ions of the type $NO_3^-(HNO_3)_m$ for m = 0 (mass 62), and m = 1 (m125). Spectrum 2c (flight of 16 April 1997 when liquid SAW-droplets where injected into the plume and when FSC was low) contains the reagent ions and in addition also the expected SA-signatures HSO_4^- (mass 97), $HSO_4^-(HNO_3)$ (m160), and $HSO_4^-(H_2SO_4)$ (m195). The identity of the peak at 150 amu is not clear, the signature at m143 stems from $NO_3^-(HNO_3)(H_2O)$.

Spectrum 2b was obtained inside the ATTAS plume (plume age 1.0-1.5 s) when sulfur-rich fuel was used (flight of 18 April 1997, FSC = 2700 ppmm). It contains the same SA-signatures as figure 2c. This indicates that SA was present and that the SA-concentration was much larger than outside the plume (2a). Note that other chemical species (e.g. SO_2) are not observed in the spectra since SO_2 and other species present in the plume do not react with the $NO_3^-(HNO_3)_m$ reagent ions. The NO_2 passed through the ion source not only produces NO_3^- ions but scavenges OH radicals and converts these to HNO_3. Therefore no additional H_2SO_4 is formed in the flow reactor from OH formed by the discharge burning in the ion source. This was checked in the laboratory for even much larger concentrations of SO_2, NO, and H_2O than expected in the plume. A measurement of gaseous SA during the flights was not performed by the VACA instrument since it would have taken too much time to cool down the flow reactor tubing.

Figure 3 shows lower limits of ambient total SA inferred from VACA data obtained during the flight of 18 April 1997. Also given are the flight altitude and the distance d between the ATTAS and the Falcon. In the background atmosphere outside the exhaust plume of the ATTAS, SA is around 15 to 50 pptv. During penetration of the sulfur-rich plume of the ATTAS (figure 3) the measured SA-concentration increases very markedly. The time plots in the two lowermost panels show a strong correlation of the total H_2SO_4 with ΔCO_2 and ΔT in all phases of plume penetrations. In an enlargement (not shown) one can see that every detail of fluctuation can be observed in each of the three measured quantities.

The lower limit conversion rate of fuel sulfur to SA can be derived by using $\varepsilon = (EI_{CO_2}\ r_{\Delta H2SO4}\ M_S)/(EI_S\ r_{\Delta CO_2}\ M_{CO_2})$. Here $EI_{CO_2} = 3,150$ g/kg fuel, $EI_S = 2.7$ g/kg fuel, $M_{CO_2} = 44$ g/mole, and $M_S = 32$ g/mole is used and $r_{\Delta i}$ represents the volume mixing
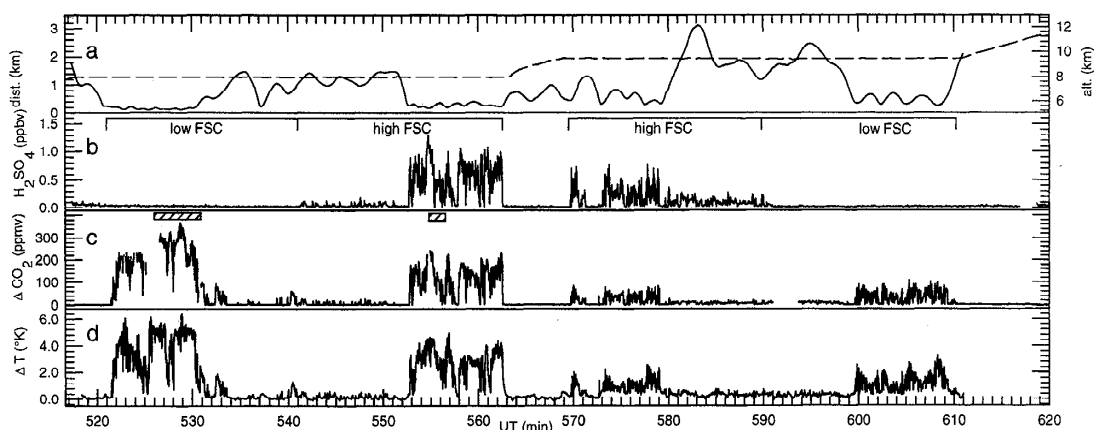

Figure 3. Time plots of the horizontal distance d between the two aircraft (solid curve, panel a), the flight altitude (dashed curve, panel a), lower limit of the total sulfuric acid volume mixing ratio (panel b), ΔCO_2 volume mixing ratio (panel c), ΔT (panel d), time intervals of low (22 ppmm) and high (2700 ppmm) fuel sulfur content FSC are indicated (panel b) as well as time intervals when CO_2 dilution was applied (shaded boxes, panel c)

ratios of ΔCO_2 and ΔH_2SO_4. Linear regression of all data obtained during sulfur-rich plume penetration periods yields a value of 4.0×10^{-6} for the ratio $r_{\Delta H_2SO_4}/r_{\Delta CO_2}$ with a correlation coefficient of 0.79. From this a mean ε of 0.34 % is calculated.

During the "SA-injection"-flight ΔT was also measured (unfortunately no CO_2 data was obtained due to a power failure) but the correlation between SA and ΔT was by far not as good as during the flight of April 18. Again it is emphasized that the formation of relatively large H_2SO_4 droplets which are not sampled by the VACA air inlet is likely and therefore additionally to the loss processes discussed above a large fraction of the expected SA may not be detectable. On the other hand it has to be taken into account that diffusional losses for large particles are much smaller than for very small particles. Therefore the potential losses of SA during the "measurement" flight of April 18 where SA may preferably be associated with very small SAW- or soot particles can not be quantified by this type of calibration.

During penetrations of the sulfur-poor plume the SA-concentration did not increase significantly above the local atmospheric background-level of 15-50 pptv. This is expected since the fuel-sulfur content of 22 ppmm was 123 times smaller than in the sulfur-rich case. Assuming the same conversion efficiency for both cases even at very young plume ages in the core of the plume an enhancement of less than 10 pptv would be expected which we were not able to distinguish from background fluctuations and statistical scatter.

Summary and Conclusions

Direct detection of total sulfuric acid (SA) has been achieved for the first time in the plume of a jet aircraft in flight. The measurements show the same SA signatures for the case when SA was injected directly into the exhaust jet and the case when sulfur was provided to the engine with the fuel. Evidence was obtained that part of the sulfur initially contained in the fuel experiences conversion to SA. A strong correlation of SA with ΔCO_2 and ΔT was observed. Our data indicate a lower limit for the efficiency ε for fuel-sulfur conversion to SA of 0.34 % inferred from the correlation with CO_2 measurements. For a fuel-sulfur content of 22 ppmm, the SA abundance does not exceed background values.

Future measurements in aircraft plumes should include simultaneous measurements of gaseous SA and total SA, measurement of different engine types, fuel sulfur contents and atmospheric conditions as well as measurement at larger plume ages. We hope to achieve fully quantitative measurements of total SA by using an advanced VACA instrument, performing further laboratory studies and in-flight calibrations

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