

SURFACE ACETONITRILE NEAR TUCSON, ARIZONA

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Abstract. Eighteen measurements of acetonitrile have been made at two rural sites about 40 km from Tucson, Arizona. Mean mixing ratio was $56 (\pm 20)$ ppt; no value greater than 84 ppt was observed. Limit of detection was between 10 and 20 ppt. Allowing for some contamination from Tucson, the results are compatible with observed stratospheric mixing ratios, small tropospheric loss, and a small global surface source.

Introduction

The presence of acetonitrile in the stratosphere has been inferred by a variety of investigators [e.g., Henschen and Arnold, 1981; a listing of other stratospheric measurements is given in Brasseur et al., 1983], and questioned by at least one [Ballenthin, 1983]. Most observations gave a mixing ratio that typically decreased with height from about 3 ppt at 25 km to about 0.5 ppt at 40 km. Tropospheric and ground sources (e.g., combustion) were considered most likely. A recent surface measurement of acetonitrile [Becker and Ionescu, 1982] yielded values of about 5 ppb in Northern Germany. Since then, it has been pointed out [Brasseur et al., 1983] that these two sets of measurements are incompatible unless there is both a large (> 100 Tg/yr) surface source and a tropospheric sink of acetonitrile. Tropospheric loss, however, seems likely to be small; the gas is not particularly soluble, its reaction rate with OH is not large [Harris et al., 1981; Fritz et al., 1982] and it should not be readily photolyzed. Brasseur et al. [1983] calculated that, with OH-mediated loss alone, and with a rate constant as found by Harris et al. [1981], the stratospheric results imply an expected ground-level concentration of about 10 ppt. Using the rate constants of Fritz et al. [1982], by extrapolation, the ground-level concentration should be closer to 20 ppt. This note reports some ground-level measurements of acetonitrile at rural sites in the Southwestern United States, which can be compared with these calculations.

Method

The measurements reported here were taken in late August and early September of 1982. Samples were collected at approximately 1.5 m above the ground, using the condensation sampling technique of Farmer and Dawson [1982]. About 60 ml of condensate were collected over periods of approximately 2 hours; data reported here are therefore 2-hour averages. About half the samples were taken during the day and half during the night; there was no significant difference. Since

acetonitrile is not very soluble (Henry's Law coefficient ≈ 165 moles l^{-1} atm $^{-1}$ at 0°C), the condensates needed to be preconcentrated; this was done by a microdistillation/trapping technique, employing an internal standard. During distillation, head-space from above the slowly rising vapor-liquid boundary was recirculated at 30 ml/min for 20 min through a porous polymer trap at room temperature with a reciprocating glass syringe pump and valves. Trapped organics were thermally desorbed (125°C) and swept with 25 ml of nitrogen into a heated, teflon-lined, 20 ml sample loop of a Hewlett-Packard 5710A gas chromatograph, equipped with flame ionization detector. A 240 cm x .15 cm I.D. teflon-lined aluminum column packed with 160 cm of Porapak QS and 80 cm Porapak S, mesh size 80/100, was used for analysis. Optimum performance was obtained with a temperature program: 90°C for 0.3 min, 16°C/min for 6 min, and 190°C for 15 min. Peak areas, retention times, and standard comparisons were registered on a Hewlett-Packard 3390A integrator.

Under the above conditions, acetonitrile was a small peak (identified by retention time and its variation with temperature) following immediately after a very much larger ethanol peak, by which it would be swamped in more contaminated environments.

The distillation and analysis steps were checked frequently with standard calibration solutions of concentration similar to the condensates. Vapor standards were produced by static dilution. Henry's Law constants at condensation collector temperatures were required and were determined from head-space analysis of thermostatted dilute solutions. Further details of the method will appear in a later paper on other organic species.

Sites

Eighteen samples were taken in all; fourteen were from the Santa Rita Experiment Station, elevation 1.3 km, in the foothills of the Santa Rita Mountains, 52 km south of Tucson, AZ. The site is remote from obvious anthropogenic influences, and the vegetation is undisturbed. Later in September 1982, samples were taken at the crest of the Santa Catalina Mountains, elevation 2.9 km, 27 km north of Tucson. Both sites are surrounded by forests of juniper and ponderosa pine.

Greater Tucson has a population of about 500,000, with no significant pollution sources other than automobiles. Southern Arizona is dotted with isolated copper smelters, which emit substantial quantities of SO₂.

Theory

A clean surface cooled below the dewpoint collects condensation which can be analyzed for

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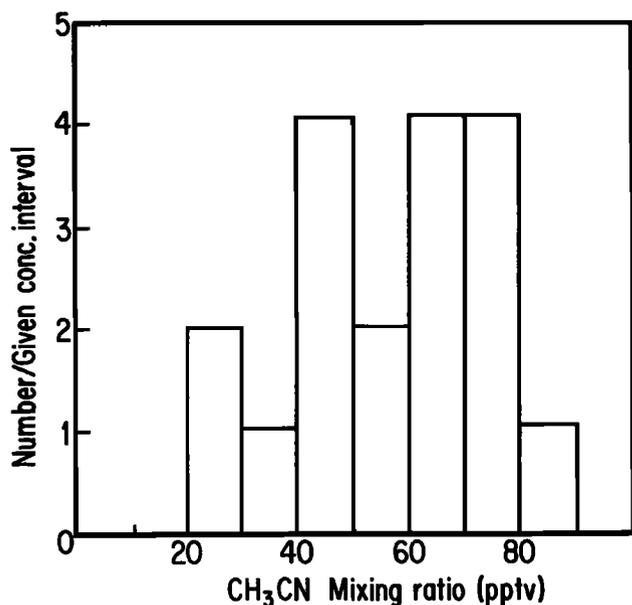


Fig. 1 Histogram of CH₃CN mixing ratios observed.

acetonitrile. The ambient vapor density of acetonitrile, ρ_{aero} , can be related to the dimensionless (mass) aqueous concentration C_a in condensate by the expression:

$$\rho_{\text{aero}} = C_a \left[\frac{B_v D_v}{B_a D_a} (\rho_{\text{vwo}} - \rho_{\text{vw}}) + \frac{1}{H_a} \right], \quad (1)$$

where D_v and D_a are the molecular diffusion coefficients of water and acetonitrile, respectively; B_v and B_a are related to the convective boundary thicknesses of the two vapors; ρ_{vwo} and ρ_{vw} are the vapor densities of water in the free air and just above the liquid surface; H_a is a Henry's law coefficient for acetonitrile, $H_a = \lim_{C_a \rightarrow 0} (C_a / \rho_{\text{aw}})$, where ρ_{aw} is the vapor density of acetonitrile just above the liquid surface. For further details of the theory and method, see Farmer and Dawson [1982]. All terms on the right-hand side of (1) can be evaluated, and therefore ρ_{aero} can be determined.

Results

A histogram of the observed results is given in Figure 1. While the number of measurements is very small (and none further are planned), it is sufficient to show that levels lie in the 50 ppt rather than the 5 ppb range. Limit of detection was between 10 and 20 ppt, depending on ethanol content of the samples. In no sample was acetonitrile undetectable. Mean mixing ratio was

56 ± 20 ppb. We were unable to obtain similar data in Tucson itself because of overlap from the very large ethanol peak on the chromatograms. However, Tucson must surely be a source of acetonitrile and will undoubtedly contaminate the measurement sites somewhat. Our data, then, are consistent with a ground-level continental-background acetonitrile mixing ratio of certainly less than 55 ppt, and perhaps less than 20 ppt.

Conclusions

On the basis of the relatively few measurements presented here, it is not necessary to invoke large global surface sources and tropospheric sinks of acetonitrile. Wet deposition should also be very small because of the low Henry's law coefficient.

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