

Application of an improved method for measurements of gaseous nitric acid in the nonurban atmosphere

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Summary. A modified filter technique to separate particles and gaseous HNO₃ is described, which is based on the use of filters of the Millipore FPLG type in combination with a virtual impactor. It enables routine measurements of gaseous HNO₃ in the atmosphere at background levels. Some results of measurements both in the marine background and over rural and semi-rural continental regions are presented.

Introduction

The major final oxidation product of NO_x is nitric acid. Incorporation in aerosols and fog, cloud and rain droplets as well as dry deposition are the dominant sink mechanisms for HNO₃. Therefore nitric acid can contribute to the acidity in aerosols, cloud droplets and rain. In the remote atmosphere the mixing ratios of HNO₃ often are only around some ten pptv to a fraction of one ppbv. In general tropospheric air also contains a substantial excess (in general a factor 3–10) of nitrate on aerosol particles [1, 2]. There exists a substantial number of measuring techniques for HNO₃ in the atmosphere. They range from tunable diode lasers [3] and laser-photolysis fragment-fluorescence [4] to simpler, classical techniques such as denuders [5, 6] and filter packages with nylon filters [1, 2, 7]. Most measurements in the troposphere are made using nylon filters combined with a Teflon prefilter and subsequent classical wet chemical analysis in the laboratory. This technique is inexpensive and relatively easy to use for routine measurements. On the other hand, sampling of gaseous HNO₃ on filter packages may be affected by nitric acid loss or formation processes due to chemical reactions on the prefilter. In this paper a modified filter technique is described which enables routine measurements of gaseous HNO₃ in the atmosphere at background levels. Some results from measurements both in the marine background and over rural and semi-rural continental regions are presented.

Experimental

The sampling technique is similar to a procedure described previously [2, 7, 8] but has been modified to improve the detection limit and to reduce interferences from aerosols. A schematic drawing of the sampling system is shown in Fig. 1. Gaseous nitric acid was collected by pumping air (100 l STP/min) through a filter stack (Fig. 2) which consists of a

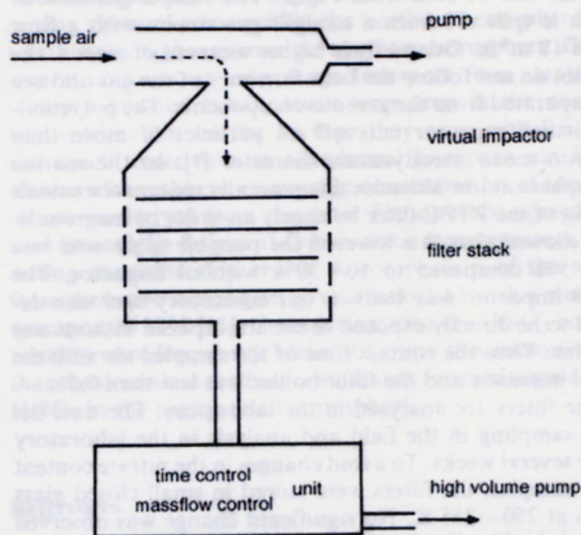


Fig. 1. Schematic drawing of HNO₃ sampling system

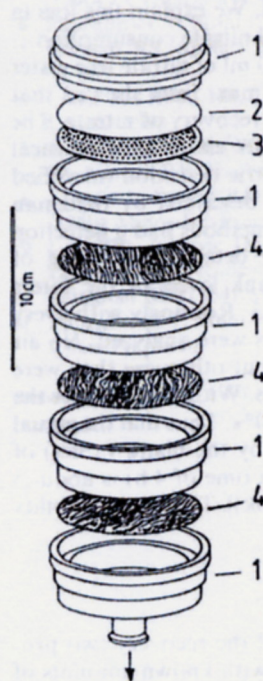


Fig. 2. Diagram of filter stack. 1: distance rings, 2: PTFE filter 3: PTFE coated filter support 4: nylon filters

PTFE filter (Millipore FGLP) with a nominal pore size of 0.2 micron followed by three nylon filters. The PTFE filter is needed to remove the particulate nitrate, the nylon filters absorb gaseous HNO_3 . The preparation of the nylon filters is modified. The filters are thoroughly washed with an aqueous solution of sulfanilamide (0.1%) and dried without any further treatment. This resulted in low and very reproducible blank values (see below) and simplified the extraction of the filters. The serial filter scheme allows the routine check of the HNO_3 sampling efficiency.

To reduce the negative interference caused by the reaction of sea-salt aerosols collected on the PTFE-filter with HNO_3 (see below) a virtual impactor was installed in front of the filter system. The principle of operation of a virtual impactor can be seen from Fig. 1. The sample gas flow of $6 \text{ m}^3/\text{h}$ is split off from a straight gas stream with a flow rate of $18 \text{ m}^3/\text{h}$. Due to their higher moment of inertia, the particles do not follow the bent flowlines of the gas and are thus separated from the gaseous components. The polyethylene virtual impactor cuts off all particles of more than 1 micron mean aerodynamic diameter [9]. In the marine atmosphere at low altitudes this generally reduces the seasalt loading of the PTFE filter by nearly an order of magnitude. Tests showed that this lowered the possible nitric acid loss to 2–5% compared to 10–30% without impactor. The virtual impactor was built in our laboratory and was designed to be directly exposed to the atmosphere without any inlet line. Thus the contact time of the sampled air with the virtual impactor and the filter holder was less than 0.1 s.

The filters are analyzed in the laboratory. The time between sampling in the field and analysis in the laboratory can be several weeks. To avoid changes in the nitrate content of the samples, the filters were stored in small closed glass vessels at 250–255 K. No significant change was observed for storage periods of 3 months. Storage tests at ambient temperature showed substantial nitrate losses within a few weeks. The loss rates varied and occasionally complete loss of nitrate within 2 weeks was found. We explain this loss in the unsterilized samples by bacterial nitrate consumption.

The filters were extracted with 20 ml of nitrate free water in an ultrasonic bath for about 20 min. Tests showed that this procedure allowed quantitative recovery of nitrate. The liquid phase was analyzed for nitrate either by a classical wet chemical method and photometric detection (modified Griess reaction similar to the one described by Saltzman [10]) or ion chromatography. Both methods had a detection limit of 2 ng/ml. This allowed the detection of 40 ng of nitrate per filter. However, the blank levels of the filters exceed this value by a factor of 2–3. Routinely with every HNO_3 measuring series blank filters were analyzed. No air was pumped through these filters, but otherwise they were handled the same way as the samples. Within each series the blanks varied typically by less than 30%. Thus that the actual overall detection limit (determined by the blank values) of the filters in 24 m^3 of air (collection time of 4 h) is about 5 pptv of HNO_3 [blank plus 3σ of blank]. The reproducibility of the method is better than 10%.

Efficiency and interferences

To test the collection efficiency and the recovery two procedures for loading the filter packs with known amounts of HNO_3 were applied. The first used the evaporation of a known amount of liquid HNO_3 in a constant gas stream.

The second was a dynamic gas dilution system combined with a HNO_3 permeation source designed and built by ECN at Petten/NL. The applied HNO_3 concentrations were comparable to ambient levels.

The total recovery of HNO_3 was better than 98% and more than 95% were collected on the first of the nylon filters. Several atmospheric constituents were tested for possible interferences. Gas mixtures containing between several ppbv and 10 ppmv of N_2O , NO_2 , NH_3 , SO_2 and PAN were passed through the filter system with flow rates and sampling periods similar to ambient air analyses. The relative humidity could be varied between 5 and 98%. No significant loss of HNO_3 or formation of HNO_3 artifacts was observed.

Also the possible influences of aerosols collected on the PTFE filter were checked. Ten PTFE filters were loaded with continental aerosols and another ten with marine aerosols. The amount of the test aerosols corresponded to a 24 h sampling time, this means is 4 to 6 times the volume usually sampled under background conditions. For continental aerosols no changes could be seen, but for seasalt aerosol a 10 to 30% reduction in the HNO_3 content of a test gas passed through the filter was found. The installation of a virtual impactor in front of the filter package reduced this interference by roughly an order of magnitude (see above). The remaining losses of 2–5% are acceptable within the overall accuracy of the method.

We have made no tests with filters loaded with artificial mixtures of ammoniumnitrate, but several tests with filters loaded with continental aerosols (up to 500 μg of nitrate per filter) were made. For Millipore FGLP filters no detectable enhancement of the HNO_3 concentration in test gases passed through these filters were found, even if the test gases were loaded with additional sulfuric acid aerosols (up to 130 μg per filter). Less favourable results were found if aerosol loaded Nucleopore filters were tested. In this case significantly enhanced HNO_3 concentrations were observed. This different behaviour is most probably caused by the different pore structures of the two filter types. Electron microscope images from particle loaded filters indeed showed very different results. For Millipore filters a uniform coverage with generally isolated particles was seen, whereas Nucleopore filters showed small islands of very dense particle coverage.

These test results indicate, that for moderate and low pollution levels the use of filters of the Millipore FPLG type in combination with a virtual impactor to separate particles and gaseous HNO_3 is adequate for the marine atmosphere and continental regions of low and moderate pollution levels. However, we have no experience for regions of high pollution levels where high loading of the particle filter may occur in spite of the virtual impactor.

Results

A detailed presentation and discussion of the results obtained with this method is beyond the scope of this paper. To demonstrate the applicability of the procedure both for measurements in the remote background atmosphere and for routine monitoring in continental areas two examples of extensive measurement series are presented. In a remote rural area near Jülich/FRG time series measurements of HNO_3 were performed during the years 1982 to 1984. Samples were collected twice a day. Day-time measurements were made between 10:00 and 16:00 CET, the night-time

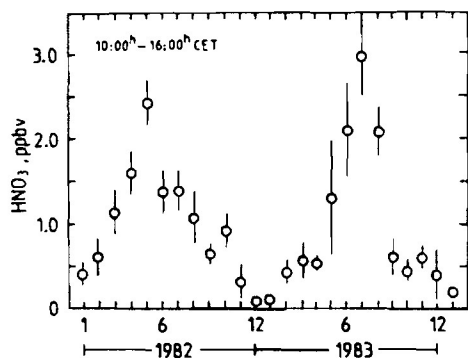


Fig. 3. Monthly means of HNO_3 mixing ratios, day-time measurements

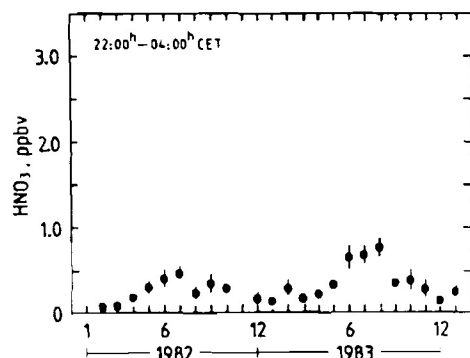


Fig. 4. Monthly means of HNO_3 mixing ratios, night-time measurements

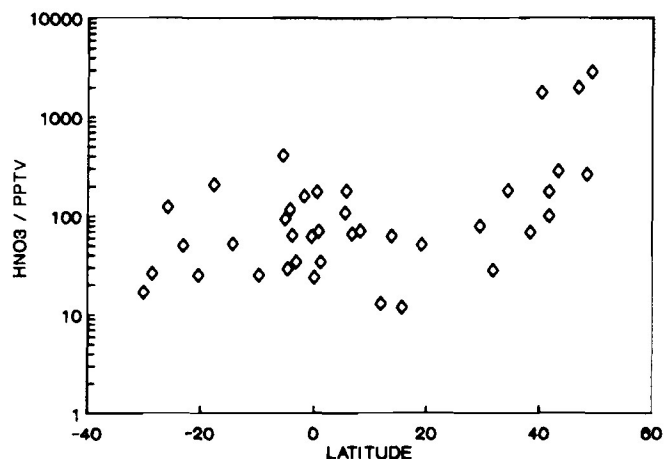


Fig. 5. HNO_3 mixing ratios measured during a ship cruise over the Atlantic in September/October 1988 (Polarstern cruise ANT VII/1)

measurements between 22:00 and 4:00 CET. The monthly means of the HNO_3 mixing ratios are shown in Fig. 3 and Fig. 4 separately for day- and night-time measurements. Each of the points represents the mean of the 20 to 25 datapoints. The day-time measurements show a significant annual variation with mixing ratios exceeding 2 ppbv of HNO_3 during summertime and less than 0.5 ppbv in winter. The night-time data show a qualitatively similar picture but the HNO_3 mixing ratios are on the average by a factor of 5 lower.

Another data set from an area with much lower HNO_3 mixing ratios was obtained during the cruise ANT VII/1 of RV "POLARSTERN" over the Atlantic from Bremerhaven/FRG to Rio Grande/Brazil (from about 50° N to 30° S). The results are shown in Fig. 5 as a function of latitude. The mixing ratios of nitric acid in the northern hemisphere were significantly higher than in the southern hemisphere. During several episodes of long range transport from continents strongly elevated HNO_3 levels were seen in the northern hemisphere. But on the average they were with 0.2 ppbv still much lower than in continental European air. In the southern hemisphere an average concentration of less than 30 pptv is derived from the data. These results agreed with laser-photolysis fragment-fluorescence measurements made during the same ship cruise. A comparison of the results from these two techniques gave a ratio 1.13 with a standard deviation of 28% [11]. Considering, that the HNO_3 concentrations were frequently below 0.1 ppbv this demonstrates, that the described method is sufficient for measurements of HNO_3 in the background atmosphere.

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