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A lab above the clouds (I)
NO_2 measurements at the Sonnblick Observatory

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Abstract

A discontinuous method for measuring nitrogen dioxide (NO_2) on a daily average basis is to be adapted to the background ambient at the Sonnblick Observatory. Originating from the basic Saltzmann method (Saltzmann 1954) it uses a solid sorbent, based on the findings of Ferm et al. (1984) consisting out of sodium iodide (NaI) and sodium hydroxide (NaOH).

Keywords

Background measurements, nitrogen dioxide, Sonnblick Observatory, daily average, air chemistry

Introduction

With its location in the remote mountainous regions of the Alps, the meteorological observatory on Mt. Sonnblick (SBO) offers a great opportunity for scientific research. Built in 1896, the station's main task was monitoring the weather. But since 1980 it also became one of the most important platforms for atmospheric chemistry, hosting a large number of projects. A high elevation background site, with a full infrastructure, situated in a region of negligible local emissions in central Europe is unique and of great value.

With the introduction of the Global Atmosphere Watch program (GAW) by the World Meteorology Organization (WMO) in 1989, and the DACH-association, a cooperation between the German stations of Hohenpeissenberg (MOHp) and Zugspitze, the Swiss Jungfraujoch (JFJ), the Sonnblick observatory has proven itself on international standards.

Because of the high altitude (3106m) the site is not affected by changes in the boundary layer but only by long-distance transport of pollutants. This allows monitoring of emissions, cloud formation, acid rain and aerosols, with the information obtained being a true indicator on the background situation in central Europe.

The collected data is used for research on climate change and the anthropogenic greenhouse effect.

Aim of the project

The aim of the project is to determine the concentration of nitrogen dioxide on a daily average basis at the Sonnblick Observatory, using the NaI-method based on the findings of FERM et al. (1984) and SALTZMANN (1954).

A method for continuous measurement is in planning. As this method is only able to detect NOy (the sum of NO_2 and other nitrous components that can be oxidized), there is the need for a reference method, which selectively monitors the NO_2 concentration.

Also included are a validation of the NaI method, the determination of its analytical parameters, especially the level of detection, and finally the evaluation of its usefulness on Mt. Sonnblick.

Methods

Before the usage of continuous monitors, the first reliable method for measuring NO_2 was the Saltzmann technique (SALTZMANN, 1954), which is a wet chemical method. It uses a bubble flask with a cylindrical frit containing the Saltzmann solution, a mixture of N-(Naphtyl-1-)ethylendiammoniumdichlorid (NEDA) and Sulphanilamin. Air is pumped through the frit and NO_2 reacts with the fluid, forming a purple azo dye. The concentration is determined through photometrical analysis.

FERM et al. (1984) separated the sampling from the analytical part by introducing a method using a solid sorbent.

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This not only evades the problems of evaporation of fluid, and mailing, but also reduces the interference of ozone because it shortens the contact time between air and sorbent.

A 3mm thick sintered glass filter with a diameter of 25 mm and a porosity of 40-60 µm is enclosed in a glass tube with hose olives at both ends. It is coated with a mixture of sodium hydroxide (NaOH) and sodium iodide (NaI) which is more sensitive to lower humidity than potassium iodide (KI).

Air is pumped through the vessel and the NO_2 is absorbed by the NaI and converted to sodium nitride ($NaNO_2$). The iodide also prevents the nitride (NO_2^-) from oxidizing to nitrate (NO_3^-).

After sampling the glass vessels are sealed and sent back to laboratory in Vienna. There the coating is washed off and turned into the azo dye by adding NEDA and Sulphanilamin. The absorption of light at 540 nm is proportional to the concentration of NO_2 and can be measured in a photometer.

The Setup

The whole setup is placed indoors. A 6x4 Teflon tube is attached to the main manifold of the station followed by a prefilter (Whatman 40), which is used to separate particulate matter. Next to the glass vessel (frit) the pump is placed followed by a gas meter. Temperature and pressure of the exhaust are measured and used for the calculations. (see Fig. 1)

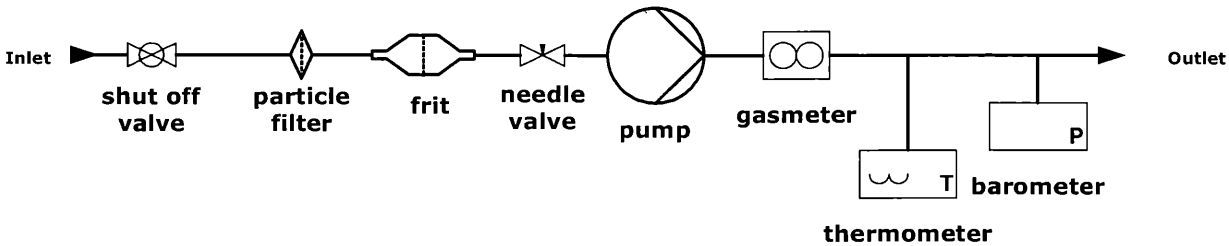

Fig. 1: The sampling setup used on Mt. Sonnblick

Results and discussion

Sampling on Mt. Sonnblick commenced in the end of September 2004, continued in November, December and January 2005 until the most recent series, which lasted through the whole month of March.

In city sites in Salzburg, for example at the Hagerkreuzung in Hallein NO_2, concentrations are at about 55 ppb daily average, in contrast to more rural areas like Hallein Winterstall or Vienna Schafbergbad (both ~5 ppb). In central Vienna they usually range up to 80 ppb, but have also reached maximum levels of 120 ppb.

On Mt Sonnblick 78% of the time measured the NO_2 concentration is below 0.3 ppb and 35% of the time even below 0.1 ppb, which is next to nothing (~$1/1000^{th}$) compared to the values found in city areas. (see Fig. 2)

And even though the numbers lie near to the limit of detection (0,028 ppb), which is obtained through field blanks, nearly all of them are above it.

During the whole time a lot of effort has been taken to improve the performance of the method; on one hand by trying to increase the flow rate, and on the other hand by enlarging the resolution of the photometric analysis. The increase of the flow rate in order to sample more of the NO_2 would very much improve the signal to noise ratio.

Low ambient pressure (~700 mbar) at this altitude hampers sampling to some extent, since the flow rate has to be increased by approximately 1.45 times in order to sample the same amount of analyte as on sea level.

Especially the flow rate seems to be one of the limiting factors, due to the fact that the absorption efficiency decreases, if the rate is too high. Tests on absorption efficiency have been performed at each series and gave very good results.

Only during the sampling period in March, where the flow was increased greatly, the absorption efficiency decreased to an average of 70% (+/-20%).

And since the concentration can even drop under the current limit of detection, it is necessary to perform further tests on absorption efficiency at higher low rates which are currently in progress.

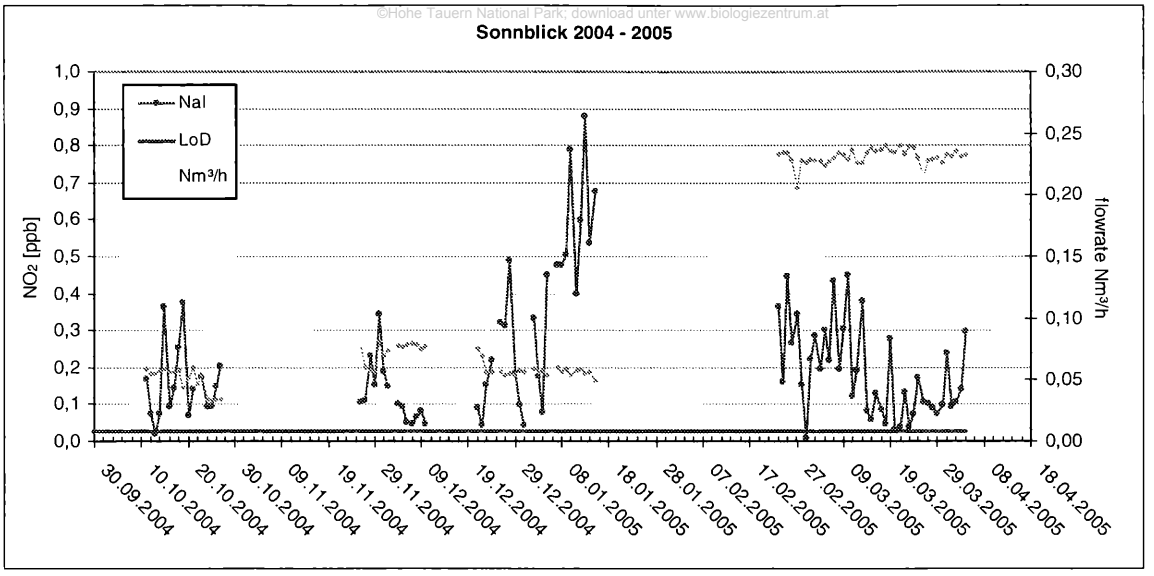

Fig.2: The measurement series on Mt. Sonnblick

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