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Atmospheric NH₃ monitoring by long-path UV absorption spectroscopy

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ABSTRACT

Differential optical absorption spectroscopy has been applied in atmospheric ammonia monitoring. The absorption of gaseous ammonia in the UV region between 190 nm and 230 nm has been examined and compared with spectra of interfering species and atmospheric transmission. A wavelength region around 210 nm was utilized in measurements of atmospheric ammonia over a 265 m path in a rural area with a detection limit of 1 $\mu\text{g}/\text{m}^3$.

1. INTRODUCTION

The distribution and fluxes of gaseous ammonia in the atmosphere are important in the study of the chemistry of acid rain, as well as the photochemistry of the atmosphere. Ammonia is the primary basic gas in the atmosphere. The significant sources of ammonia are animal waste, ammonification of humus followed by emission from soil, loss of ammonia-based fertilizers from soil, and industrial emissions.¹ Atmospheric ammonia detection and measurement are important since the concentration of ammonia is a critical parameter in the rates of formation, transport, transformation, and removal of aerosol sulphur and nitrogen compounds. Consequently, accurate monitoring methods are needed for ambient concentrations, but new measurement techniques might also find applications in areas where ammonia is being used or generated and would pose a health hazard at elevated levels. Measurements of ammonia are normally performed with wet-chemical techniques, which require the collection of atmospheric samples. Optical techniques based on long-path absorption are, in this context, an attractive method, capable of *in situ* real-time measurements.

Optical absorption in the IR region has been applied in atmospheric ammonia monitoring both passively, using absorption features in solar spectra obtained from the ground, and with active techniques, using IR₂ lamps and lasers. Solar spectra have been used to measure column abundances,² and altitude information has been³ obtained from high-resolution spectra obtained using a heterodyne radiometer.³ Pollutant concentrations close to the ground have been monitored by active Fourier Transform Infrared Spectroscopy (FT-IR).^{4,5} CO₂ lidar systems have been used in Differential Absorption Lidar (DIAL) measurements of ammonia using backscattered radiation from topographic targets.^{6,7}

The Differential Optical Absorption Spectroscopy (DOAS) technique is^{8,9} a powerful method for absorption measurements in the UV and visible regions. In the DOAS approach, a powerful broadband lamp is mounted in a reflector

arrangement at a distance of normally a few kilometres from an optical receiver system. Repetitive fast scanning of a dispersive spectrometer is carried out over a small spectral region at a rate that leaves even minute atmospheric absorption features unaffected by air turbulence. The DOAS technique has been used to monitor a wide variety of atmospheric trace gases. In the present work we have investigated the possibility of utilizing the UV spectral region in ammonia monitoring. Gaseous ammonia has a strong absorption band in the 170-220 nm region.^{10,11} Preliminary studies of DOAS applications to ammonia measurements in a part of this spectral region have been performed previously.¹² In the present study the absorption of ammonia has been examined and compared with spectra of interfering species and atmospheric transmission. A field study of ammonia employing UV-DOAS in a rural area will also be discussed.

2. EXPERIMENTAL ARRANGEMENT

In order to find the best spectral region for ammonia monitoring in the atmosphere, the absorption spectra of ammonia and interfering species, such as oxygen, sulphur dioxide, nitric oxide and nitrogen dioxide, were studied in the UV wavelength region. A 150 W xenon arc lamp (Hamamatsu L2273), which gives a broad emission spectrum in the UV and visible regions, was used as the light source. After passage through a 10 cm long quartz cell a portion of the light was focused onto the entrance slit of a SPEX 500M spectrometer (0.5 metre, f/4 Czerny-Turner). The grating used has 1200 grooves/mm and blaze at 300 nm. The normal exit slit was replaced by a rotating slotted disk to facilitate rapid scanning of a small wavelength region. The spectrum was masked in the focal plane to cover approximately 40 nm. The distance between the slits along the rim of the disk is slightly greater than the aperture of the mask, so that at any time no more than one slit is irradiated. The width of the entrance slit of the spectrometer could be varied, while the slits on the rotating disk were fixed at 100 μm . The best resolution was 0.23 nm in the central part of the spectrum and decreased to 0.53 nm at both ends of the spectrum, due to slightly tilted slits in these parts of the scan. The 23 cm diameter disk has 20 slits near the rim and rotates with a speed of 300 r.p.m., thus giving a scan repetition frequency of 100 Hz. After passage through the moving slit the light was detected in an EMI 9558 QA PMT. After amplification the signal was sent to an IBM-compatible AT computer and digitized by a high-speed 12-bit A/D converter on a custom-made multi-channel analyser card. As the exit slit sweeps over the spectral region, 1000 digitized signal samples are taken during the scan period of 10 ms. Several scans can be averaged to increase the signal-to-noise ratio. The wavelength scale of individual scans is synchronized by using the trigger signal obtained when the slit passes an infrared light barrier close to the edge of the mask.

The atmospheric spectra were recorded with the same equipment, with the lamp placed at the focus of a parabolic mirror (20 cm diameter, $f = 80$ cm) to achieve a collimated beam over a long atmospheric path. The light was collected at the other end of the path with a similar telescope, and focused directly onto the entrance slit of the spectrometer. All telescope mirrors were coated with magnesium fluoride to enhance the UV reflectance.

3. MEASUREMENTS

During most of the measurements, the grating of the spectrometer was fixed to give a central wavelength of 210 nm, and thus a rapid scan in the 190-230 nm region was achieved with the slotted disk device. The wavelength scale and resolution were calibrated with spectral lamps. Stray light from the much more intense wavelength regions of the xenon lamp was found to be a problem, especially at shorter wavelengths in the spectrum. The remedy for this was to place an interference filter, centre wavelength 201.5 nm and bandwidth (FWHM) 18.5 nm, directly in front of the PMT. An easy way of checking that there was no background interference was to record the absorption spectrum from an absorbing species with high concentration. The transmission at the line centres should then be zero. The absorption spectra of ammonia, sulphur dioxide, nitric oxide and nitrogen dioxide were recorded with different resolutions and stored for later comparison with atmospheric spectra. The quartz cell was filled with known amounts of calibration gases for these species, except ammonia, for which no calibration gas was available at the time of the measurement. The ammonia calibration sample was prepared by diluting pure ammonia in nitrogen until a suitable absorption was obtained. Due to the uncertainty in the measurement of the small partial pressure of ammonia, the concentration in the final sample was inferred by using earlier absorption cross-section determinations.¹⁰ For each species measurement a reference spectrum was recorded with an empty cell which was used to calculate the optical transmission. Fig. 1 displays the results from various concentrations of ammonia, sulphur dioxide and nitric oxide in the 10 cm long cell; 140 mg/m³, 395 mg/m³ and 1240 mg/m³, respectively. As can be seen from the figure, there will always be some interference from sulphur dioxide in ammonia monitoring. Nitrogen dioxide was also studied, but was found to have essentially continuous absorption in this spectral region with only slight differential structure, which should be negligible in normal atmospheric conditions.

The most important restriction in the wavelength choice for atmospheric ammonia monitoring arises from oxygen absorption. The Schumann-Runge bands make the atmosphere nearly opaque below 200 nm over moderate distances, but even in the region 200-230 nm there is strong attenuation, due mainly to a dissociation continuum of oxygen.¹³ The optimum pathlength for DOAS measurements of atmospheric ammonia will thus be shorter than that for other species. The oxygen absorption spectrum could not be measured in the laboratory due to insufficient reflectance of the mirrors in a White multi-pass cell used to achieve long optical paths. The structure in the oxygen spectrum was instead studied in measurements over open atmospheric paths. Two different paths were used; one 350 m long, close to the department inside the city of Lund, and one 265 m long, in a rural area 30 km outside Lund. A spectrum from the latter site is shown in Fig. 2. This shows only the differential structure in the absorption spectrum, which was obtained by dividing the raw spectrum by a fitted 5th order polynomial. This is a normal procedure in DOAS measurements used in order to remove the underlying feature due to the spectral profile of the lamp, atmospheric broadband attenuation, spectrometer transmission, detector sensitivity, etc. The narrow features caused by gas absorption are not significantly affected by this procedure. The absorption bands in the lower part of the spectrum in Fig. 2 are due to

oxygen, whereas the wavelength region 208-218 nm seems to be free from stronger absorption lines. The smaller features in the upper part of the spectrum are, in this case, due to ammonia absorption. These wavelengths were not affected by strong interference, except sulphur dioxide and nitric oxide, even for the urban path.

The rural path was used to study the ammonia concentration during one week in June. The path passed 2 m above a meadow. The ammonia content could be affected by a chicken farm, located about 1 km from the measurement site, during certain wind conditions. Fig. 3 shows an example of a spectrum used for the determination of the ammonia concentration. This is derived from the same raw spectrum as that shown in Fig. 2, but with a polynomial fit only over the interesting region. The atmospheric spectrum is compared with an ammonia absorption spectrum from the laboratory studies (dotted curve) with the same resolution and the same type of polynomial fit. The concentration is extracted by performing a least-squares fit of the observed absorption spectrum and a scaled reference spectrum, yielding an ammonia concentration of $6.7 \mu\text{g}/\text{m}^3$. An even better fit can be achieved by simultaneously fitting reference spectra of sulphur dioxide and nitric oxide. The inferred concentrations of these species in this example were $1.0 \mu\text{g}/\text{m}^3$ and $0.3 \mu\text{g}/\text{m}^3$, respectively, with an overall correlation coefficient for all three species of 0.99. The degree of correlation for the individual species can be used to deduce the standard deviation in the concentration measurements. The concentration of ammonia during the week ranged from below the detection limit up to $22 \mu\text{g}/\text{m}^3$. The detection limit for 15 minutes integration time, which was used throughout the measurement, was normally around $1 \mu\text{g}/\text{m}^3$, depending on the atmospheric conditions and the degree of interference.

4. CONCLUSIONS

DOAS measurements in the UV region have been shown to be useful in atmospheric ammonia monitoring. A wavelength region around 210 nm was found to be suitable in terms of interference problems and atmospheric transmission for pathlengths of 200-400 m. The main sources of interference are absorption by sulphur dioxide and nitric oxide, which can be removed by deconvolution in the data processing for most atmospheric conditions. The detection limit for ammonia in the present study was found to be $1 \mu\text{g}/\text{m}^3$. It should be possible to improve this limit by using a better optimized system. The detected light intensity (or the atmospheric path) could be increased by using a lamp with a higher luminance, a better blazed grating and an optimized interference filter. If the spectral profile of pure oxygen is known in detail it might be possible to extract ammonia concentration data from some of the stronger bands at shorter wavelengths. Further studies of this kind are in progress, including field campaigns involving comparative measurements with other techniques.

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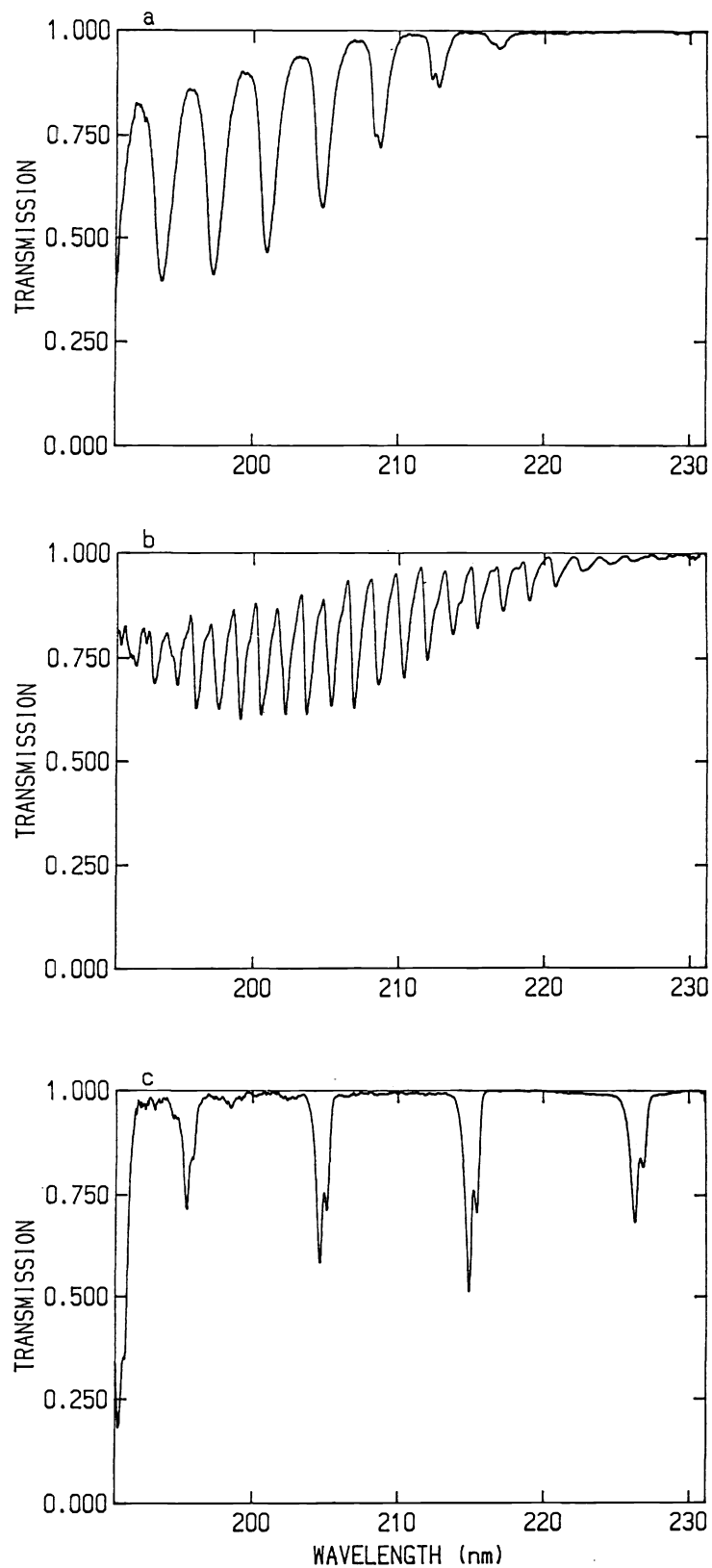


Fig. 1. UV absorption spectra of a) ammonia, b) sulphur dioxide, and c) nitric oxide.

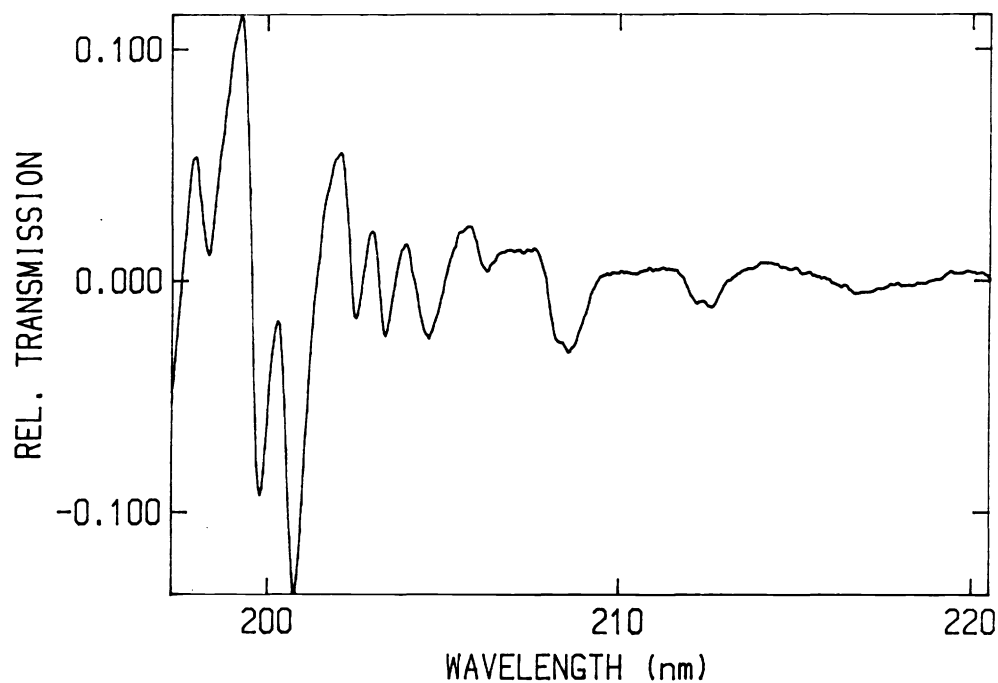


Fig. 2. Differential absorption spectrum of a 265 m atmospheric path.

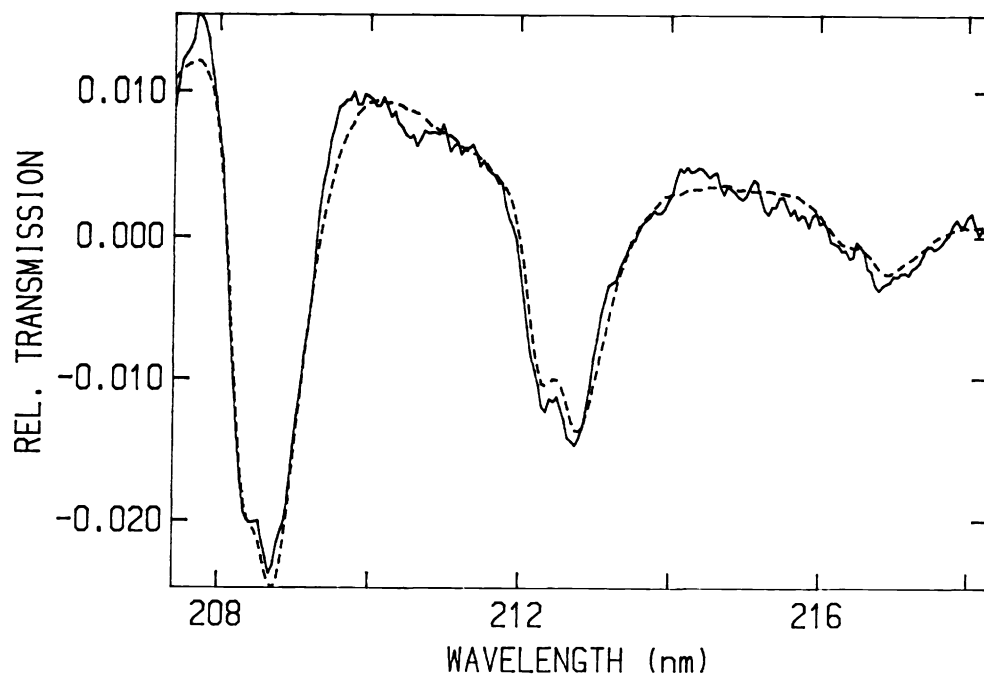


Fig. 3. Differential absorption spectrum used for the determination of the atmospheric ammonia concentration (ammonia reference spectrum inserted as a dotted curve).