

Temperature Dependence of the Absorption Spectra of Nitrogen Oxide, Nitrogen Dioxide and Sulfur Dioxide in the Application of Differential Optical Absorption Spectroscopy*

J. Mellqvist† and A. Rosén

Department of Physics, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

H. Axelsson

Swedish Environmental Research Institute (IVL), P.O. Box 47086, S-402 58 Göteborg, Sweden

An experimental set-up has been designed for measurements of differential absorption cross-sections of gases at different temperatures. Preliminary measurements on NO, NO₂ and SO₂ have been carried out at temperatures between 20 and 400 °C by using spectral resolutions in the range 0.26–0.95 nm. These measurements show that the differential absorption cross-sections for all three gases decrease continuously with increasing temperature. Large relative errors resulted when differential absorption cross-sections obtained at room temperature were used in the differential optical absorption spectroscopic technique for evaluation of the concentration of gases at high temperatures. The relative errors were of the order of 70% for SO₂ and NO₂ and of the order of 20% for NO at 400 °C.

Keywords: Differential absorption; nitrogen oxide; nitrogen dioxide; sulfur dioxide; temperature effects

Differential optical absorption spectroscopy (DOAS) is a quantitative optical measuring technique for gases absorbing in the ultraviolet (UV) and visible spectral regions.¹ The technique is based on the recording of differential absorption, *i.e.*, the difference between local maxima and minima in the absorption spectrum of the probed gas. In the application of DOAS, the light from a broad-band xenon high-pressure lamp is transmitted through the atmosphere for distances of up to several kilometres. The light is received and analysed by use of a fast-scanning device (dispersive spectrometer) to eliminate the influence of air turbulence. The DOAS technique has been used to monitor a wide variety of atmospheric gases, *e.g.*, NO₂, SO₂, NO, NH₃, HNO₂ and O₃.² An interesting application of DOAS would be to use it for the monitoring of flue gas emissions. A straightforward application of the technique is, however, not justified as the flue gases have high temperatures, which could significantly affect the differential absorption cross-sections. In addition, the measurement pathlength is not variable, which could lead, at high gas concentrations, to a much higher differential absorption than is usually preferred (1%).

Preliminary measurements of the differential absorption cross-sections of NO, NO₂ and SO₂ in the temperature range expected in a flue gas (20–400 °C) were therefore undertaken. In this paper, the experimental equipment is described and some preliminary results are presented. Measurements were also carried out at high concentrations (large differential absorption) to verify the region of linearity of DOAS for measurements on NO, SO₂ and NO₂. These results will be published in a later paper, together with more extensive measurements and calculations of the temperature dependence of the differential absorption cross-sections.

Experimental

The experimental set-up is shown in Fig. 1. Light from a 150 W xenon arc lamp (Hamamatsu L2273) was transmitted through a 1.19 m long stainless-steel measurement cylinder

(i.d. 0.105 m) and then focused onto the entrance slit of a Jarrell–Ash spectrometer (275 mm, *f*/3.8 Czerny–Turner). The spectrometer was equipped with a rotating slotted disc set-up, replacing the exit slit.³ The measurement time for each scan of the spectrum was 10 ms. Three different gratings were used with grating constants of 2400, 1200 and 600 grooves mm⁻¹ and these were blazed at 260, 300 and 300 nm, respectively. The width of the entrance slit was 100 µm and the slotted disc on the exit side had 100 µm slits. The best spectral resolution was 0.26 nm in the central part of the spectrum. The spectral resolution decreased, however, to 0.34 nm at both ends of the spectrum owing to slightly tilted slits in these parts of the scan. The spectrum was masked in the focal plane to cover approximately 24 nm when the best resolution was used. An EMI 9750 QA photomultiplier tube was used as the detector, and the signal was amplified and passed to an IBM-compatible AT computer with a custom-made multi-channel analyser plug-in card with a 12-bit analogue-to-digital converter, dividing each scan into 100 channels. After sampling of 2×10^4 scans over a period of 5 min, the data were transferred to the computer for signal processing.

The measurement cylinder was placed in a heat-pipe oven that could be maintained in the range 20–500 °C. The temperature was measured at three places inside the cylinder,

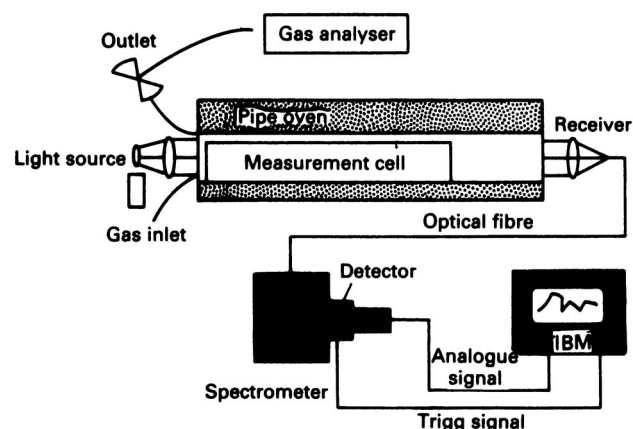


Fig. 1 Experimental set-up used for measurements of the differential absorption cross-sections of gases at different temperatures

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† Also at the Swedish Environmental Research Institute (IVL), P.O. Box 47086, S-402 58 Göteborg, Sweden.

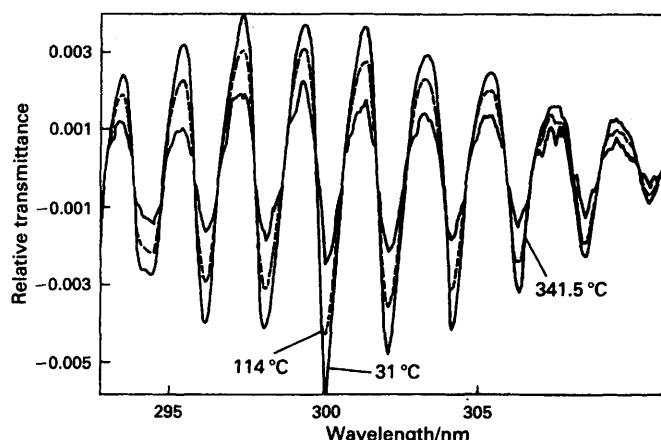


Fig. 2 Differential absorbance(a_e) of SO_2 around 300 nm at three different temperatures, 31, 114 and 341.5 °C. Resolution, 0.5 nm. The concentration is normalized to 15.00 mg m^{-3} of SO_2 in the measurement cell

at both ends and in the middle, by using type-K thermocouples. The gas was pre-heated in a stainless-steel tube (i.d. 4.35 mm) before it entered the measurement cylinder. At the outlet of the measurement cylinder the static pressure was measured by using a differential pressure gauge, together with a mercury barometer. The gases investigated were delivered from AGA in Sweden at specific volume concentrations. They were all diluted in nitrogen with a precision of 2% v/v. These gases were additionally diluted with use of a mass-flow instrument (Enviro-nics 100). The gases were analysed at the outlet of the measurement cylinder by conventional monitors. A fluorescence instrument (Monitor Laboratories 8850) was used for SO_2 and a combined infrared and UV absorption instrument (BINOS) for NO_2 and NO . The determination of the differential absorption cross-sections for NO , NO_2 and SO_2 in the application of DOAS was carried out according to the algorithms described by Platt and Perner.³

Measurements

Measurements of the differential absorption cross-sections of NO , NO_2 and SO_2 were carried out at nine temperatures between 20 and 400 °C at pressures close to atmospheric. Different spectral resolutions (0.26–0.98 nm) and gas concentrations (5–200 ppm, v/v) were used. The measurements were performed dynamically by passing gases continuously (2–8 l min^{-1}), at known volume concentrations, through the measurement cylinder. In this way, wall effects (adsorption/dissociation) were suppressed. Nitrogen oxide was measured around 226 nm, SO_2 around 300 nm and NO_2 around 430 nm. In order to avoid photodissociation of the absorption gases, optical filters were used for SO_2 and NO_2 , with cut-off wavelengths at 240 and 397.5 nm, respectively. The absolute values of the differential absorption cross-section were obtained by calculating the true number density in the measurement cell by using the ideal gas law. By correlating the differential absorption cross-sections at all measured temperatures with the differential absorption cross-section at room temperature, values of the influence of temperature on DOAS were quantified for each gas.

Table 1 Maximum relative errors (%) of the measured gas concentrations at different temperatures, obtained by using DOAS with differential absorption cross-sections determined at room temperature. The spectral resolution was 0.26 nm

Measured gas	Concentration (ppm)	150 °C	300 °C	400 °C
NO	11	7	15	20
NO_2	120	40	60	75
SO_2	6	30	50	65

Results and Discussion

The recorded experimental data show that the magnitude of the differential absorption cross-sections for NO_2 , NO and SO_2 is strongly dependent on the temperature. The differential absorbance(a_e) (differential absorption cross-section \times concentration \times pathlength) for SO_2 at three temperatures (31, 114 and 341.5 °C) is shown in Fig. 2. The concentration was normalized to 15.00 mg m^{-3} by the use of the ideal gas law. It can be seen that when the temperature increases continuously, the magnitude of the differential absorption cross-section decreases continuously, i.e., the absorption at the peaks decreases while the absorption at the troughs increases. The measured temperature dependence at 114 °C was in close agreement with that reported by Woods *et al.*⁴

Considerable errors in evaluated concentration from a DOAS measurement could therefore arise owing to the effects of temperature, as shown in Table 1. These values were obtained by using differential absorption cross-sections, determined at room temperature, for evaluation of the gas concentrations in the measurement cylinder at different temperatures. No quantitative effect was observed with variation of the spectral resolution (0.26–0.95 nm), although the correlation between temperature and magnitude of the error was more clearly defined at higher spectral resolutions. The observed temperature dependence followed a continuous function. Hence, in practice, one should be able to compensate for the temperature dependence. This would require empirically defining the temperature dependence function, and adequately monitoring the flue gas temperature. Results depicting the correlation between temperature and magnitude of the error for NO , NO_2 and SO_2 are also qualitatively verified by theoretical calculations for NO .⁵

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