



## Caution with Spectroscopic NO<sub>2</sub> Reference Cells (Cuvettes)

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Spectroscopic measurements of atmospheric trace gases, e.g. by Differential Optical Absorption Spectroscopy (DOAS) are frequently supported by recording the trace gas column density (CD) in absorption cells (cuvettes). The idea being that the proper working and the spectral registration (wavelength calibration and spectral resolution) of the instruments can be verified. Also that some kind of calibration (absolute determination of trace gas CD) can be performed. In principle, DOAS applications do not require absorption cell calibration, however in practice measurements with absorption cells in the spectrometers light path are frequently performed. In addition, trace gas absorption cells are used as a central component in gas correlation spectroscopy instruments.

Here we show at the example of NO<sub>2</sub> absorption cells that the effective CD seen by the instrument can deviate from expected values by orders of magnitude and in a surprisingly complex way. While several effects can contribute to this deviation, analytical calculations and kinetic model studies show the dominating influence of NO<sub>2</sub>-photolysis and dimerisation of NO<sub>2</sub>. In particular, this means that the partial pressure of NO<sub>2</sub> in the cell matters, however, problems can be particular severe at high as well as low NO<sub>2</sub> pressures (of the order of one bar and a few mbars, respectively). Also it can be of importance whether the cell is filled with pure NO<sub>2</sub> or topped up with air or oxygen (O<sub>2</sub>). We suggest key conditions for obtaining optimal stability and predictability of the NO<sub>2</sub> concentration in the cell.