波長変調分光法を用いた大気中一酸化炭素のリアルタイム測定装置の開発

Development of a real-time measurement device of atmospheric carbon monoxide combined with mid-infrared wavelength modulation spectroscopy

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Carbon monoxide (CO) is emitted from incomplete combustion of fossil fuels and biomass. It affects the concentration of CO_2 and CH_4 through the reactions with hydroxyl radicals. The major method of the measurements of CO is NDIR. This method is highly sensitive and highly stable. There are a lot of data of the concentration of CO measured with NDIR, but they show only hourly average. In this study, we developed a mid-IR laser absorption spectrometer that uses a 4.57 μm quantum cascade laser with wavelength modulation spectroscopy (WMS).
The absorption line for the measurements of CO was at 2190.02 cm^{-1}. The laser was scanned at 1 Hz. The beam was collimated with CaF_2 lens and introduced into the cell. The optical path length was 29.91 m. The signal from a photodetector was processed by the lock-in amplifier.
To assess signal stability and detection limit, 1.02 ppm CO gas was introduced into the WMS system. From the Allan variance plot, an optimum integration time of 145 s was derived. Averaging 145 times, the precision (1σ) of the measurement was 6.5 %.
For the measurement of the detection limit of this instrument, we collected the signal of different CO mixing ratio and made the calibration curve. From the slope and the averaged baseline deviation, the detection limit (SNR = 2) was found to be 0.094 ppm.
Measurements of outside air were conducted on the Kashiwa campus of The University of Tokyo over October 24-27, 2015.During the measurements of ambient air, the calibration was performed every 6-9 hours.
Outside air measurements were conducted over October 24-27, 2015. The CO mixing ratio during the measurements ranged from 0.097 ppm to 1.8 ppm. On the night of October 24, the concentration of CO increased continuously. The wind brew from south-southwest. In that direction, there is Keihin industrial area, so the emission from the factories in the area may have contributed to the CO mixing ratio increase. On October 25 the wind brew from northwest throughout the day. There are no big industrial areas in that direction. Car entrance was restricted because the campus was opened to the public. These may be the reasons the concentration of CO was steady and low.
We performed in situ measurements of CO mixing ratios in ambient air with a near-IR laser absorption spectrometer using WMS. We successfully detected CO mixing ratio change in the ambient air instantly.

