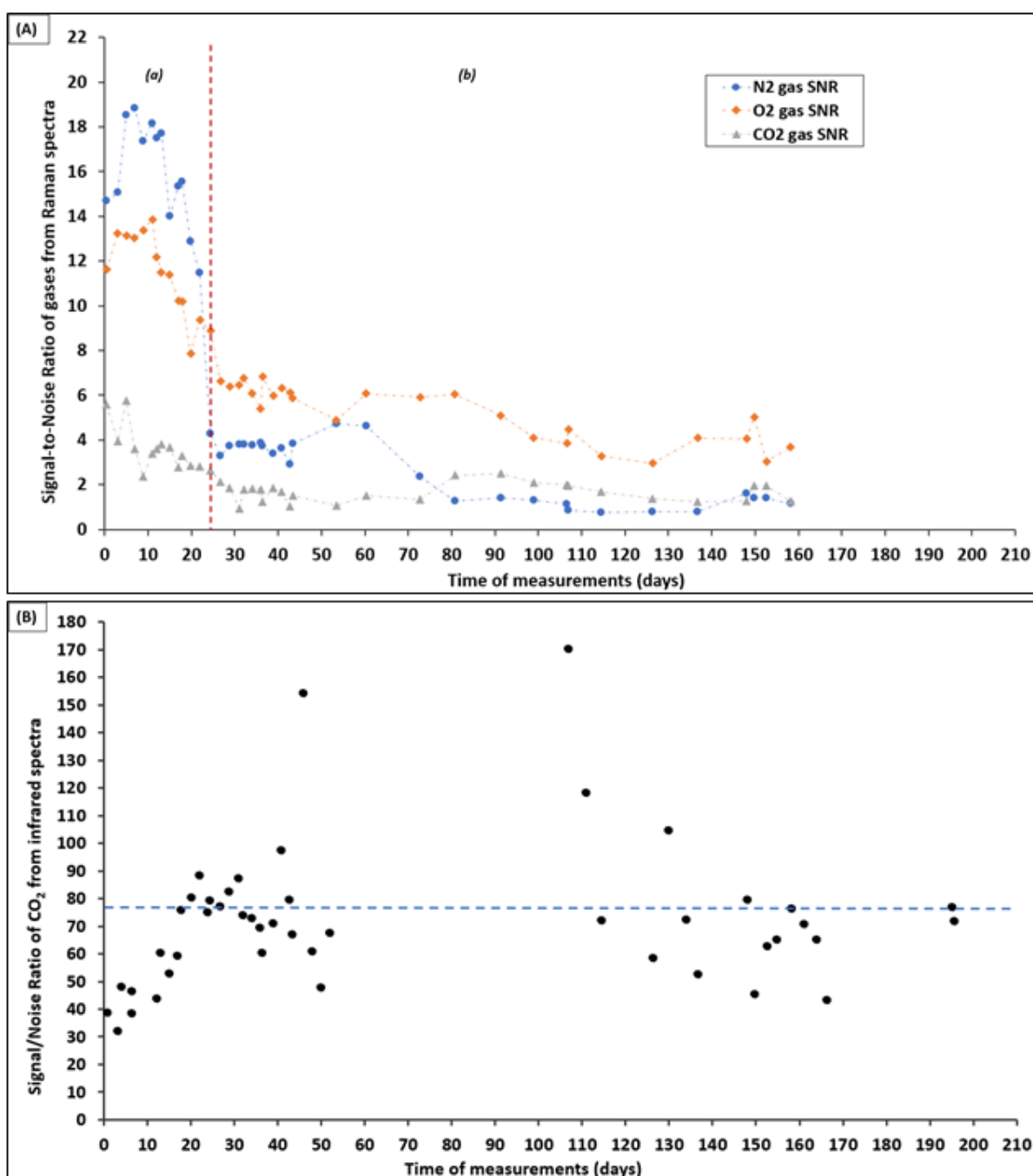## Appendix 4: Determination of the optical characteristics: Signal-to-Noise Ratio (SNR) and the instrumental derivative factor (F).

46 spectra for each technique covering the whole baseline period are selected to represent each of the sub-periods according to the following criteria:

(i) For Raman, 24 spectra distributed every two days from May 7 to June 19, 2019 and 4 selected spectra for each time period (#4-#9) from June 20 to November 19, 2019

(ii) For infrared, one spectrum selected every 2 or 4 days from May 7 to November 19, 2019.
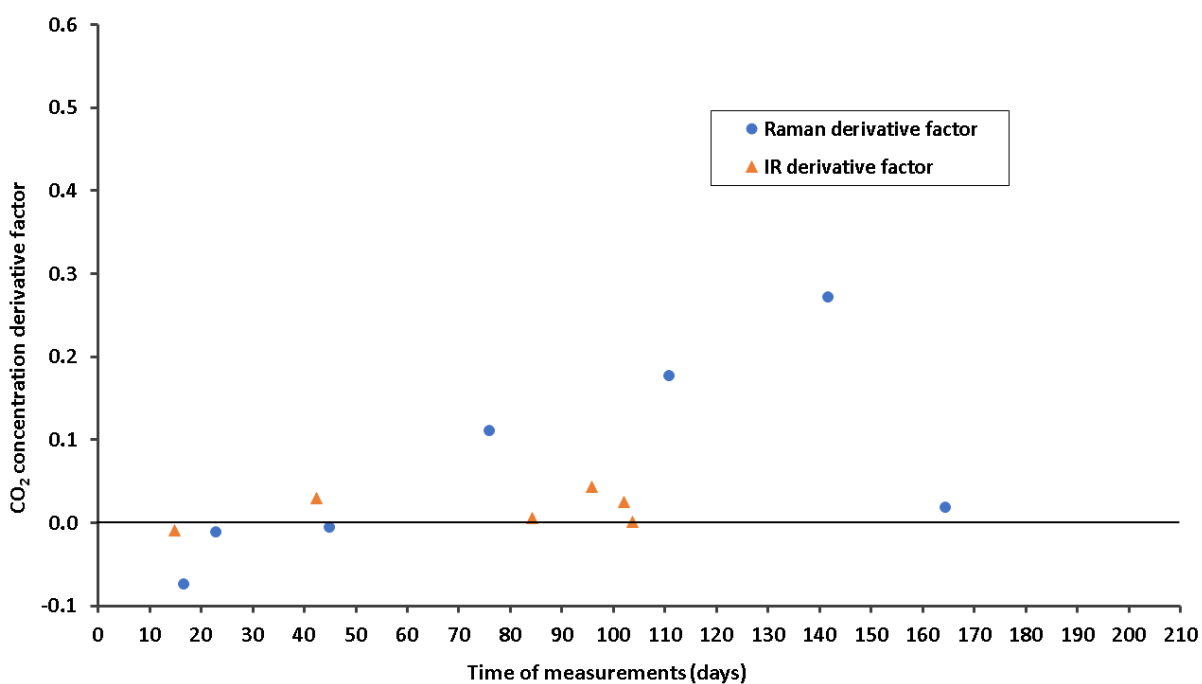
Signal-to-Noise Ratio (SNR):

Evolution of the Signal-to-Noise Ratio (SNR) of N_2, O_2 and CO_2 during the baseline period from May 7 to November 19, 2019: (A) = for 46 Raman spectra of N_2, O_2 and CO_2 (24 spectra distributed every two days from May 7 to June 19, 2019 and 4 selected spectra for each time period (from #4 to #9) from June 20 to November 19, 2019) and (B) = for 46 infrared spectra of CO_2 (spectra selected every 2 or 4 days when data exist) whose the average SNR is represented by the blue dotted line.

Derivative factor F:

$$F = \frac{\overline{[C_{CO2}]}t - X_{CO2}}{X_{CO2}} \qquad (5)$$

Where $\overline{[C_{CO2}]}t$ = average of the dissolved CO_2 concentration (in mg.L^{-1}) for each time period t

X_{CO2} = first value of the moving average of the dissolved CO_2 concentration (in mg.L^{-1}) for each time period t.

Raman (blue dots) and infrared (orange triangles) for dissolved CO_2 concentrations over a period of 203 days.