Ground-based SO$_2$ Measurements

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Measuring $\text{SO}_2$ emissions
FLYSPEC

Calibration Cells → Optics + Electronics → USB2000 → Computer

GPS receiver

Sub-notebook Computer

Telescope Spectrometer

GPS Antenna Calibration cells
USB2000 Spectrometer

The USB2000 incorporates a monochromator based on an asymmetric crossed Czerny-Turner configuration, and a 2048-element charge coupled device (CCD) linear silicon array.

Ocean Optics USB2000 Fiber Optic Spectrometer.
Spectrometer’s components: 1=SMA connector, 2=slit, 3=filter, 4=collimating mirror, 5=grating, 6=focusing mirror, 7=Optional L2 detector collection lens, 8=CCD detector.
Intensity and Transmittance

\[ I(\lambda) = I_0(\lambda)e^{-L[\Omega_S(\lambda) + \Omega_{RM}(\lambda)]} \]

\[ T = \frac{I}{I_0} \]

\[ A = -\ln(T) = -\ln\left(\frac{I}{I_0}\right) \]
Acquisition of Light Spectra

The graph shows the intensity counts as a function of wavelength in nanometers. There are three regions highlighted:

- **Light range**: 285-320 nm
- **SO₂ range**: 305-320 nm

The graph includes the following curves:

- **Reference spectrum**
- **Low calibration cell**
- **High calibration cell**
- **Dark spectrum**
2.3.2 Absorption cross-section

The absorption cross-section $A_n$ is defined as the logarithm of the ratio between a reference without the sample and transmitted through the sample intensity of light with all other conditions or variables constant. Thorburn & Smith:

$$A_n = -\ln \left( \frac{I}{I_0} \right)$$

In the laboratory, the main variables that must be controlled are temperature, pressure, and intensity of the artificial source light. Likewise, when studying volcanic plumes in the field, it is important to be aware of the changing light and atmospheric conditions. WilliamsoJones et al.

As the volcanic plume moves and disperses in an area around the vent, it is possible to measure the background atmosphere in a path length where the plume is not present. This measurement of the atmospheric background, along with the acquisition of calibration cells spectra, provides advantages when processing the spectra as radiative transfer modeling is not necessary, and most of the non-desirable scattering effects, such as inelastic Raman scattering, affecting the true molecular absorption can be separated. Horton et al.

Rearranging Equation 5 to include the effect of the light passing through the volcanic plume:

$$I(\lambda) = I_0(\lambda) e^{-L \Omega_A} e^{-l \Omega_p}$$

where $\Omega_A$ considers the general atmospheric absorption without the plume, $\Omega_S$, $\Omega_R$, and $\Omega_p$ is the molecular absorption that takes place within the volcanic plume only, and $l$ the path length (vertical thickness) of the volcanic plume. The reference light spectrum is defined as:

$$I_R(\lambda) = I_0(\lambda) e^{-L \Omega_A}$$

which must be measured away from the plume. Then combining equations 6 and 7, the absorbance profile of the volcanic plume is obtained:

$$A_{plume}(\lambda) = -\ln \left( \frac{I(\lambda)}{I_R(\lambda)} \right) = l \Omega_p$$

$$A_{plume}(\lambda) = \sigma_{SO_2}(\lambda) c_{SO_2} l$$

For $SO_2$: $1 \text{ ppm} \cdot m = 2.663 \times 10^{-6} \text{ kg} \cdot \text{m}^{-2}$ (Gerlach, 2003).
SO$_2$ absorption

![Graph showing SO$_2$ absorption spectrum]

- Wavelength range: 295 to 320 nm
- Absorbance cross-section in units of nm cm$^{-1}$

The graph illustrates the absorption peaks of SO$_2$ at various wavelengths, indicating the specific wavelengths at which SO$_2$ absorbs light most effectively.
Differential absorbance
DA Correlation

Relation between differential absorption profiles

Since in the wavelength dependent DA profile the variation in amplitude of the narrow features depends on the gas path length concentration only and that the absorptivity coefficient in Equation 2 is independent of the gas concentration, it follows that wavelengths with similar DA amplitude should have similar absorptivity coefficients. Thus, any pair of DA profiles can be correlated so that one profile can be obtained from the other through a multiplication factor \( f \) that is related to the difference in gas path length concentrations only.

\[
DA_h(\lambda) = f \cdot DA_l(\lambda)
\]

where \( DA_h \) and \( DA_l \) are the differential absorption spectra associated to a relatively high and a low gas concentration, respectively (Figure 2).

Active correlation between absorption amplitude and gas concentrations

From the calibration procedure, the DA spectra and corresponding known gas path length concentrations of the calibration cells are required to calculate the parameters of active correlation models and to obtain the unknown concentration. To perform the active correlation between DA profiles, a Bisquare Weighted Least Square (BWLSp) is applied to each pair of profiles corresponding to the new spectrum of unknown concentration and the calibration cells DA spectra. The advantage of this technique is that it minimizes the effect of outliers by iterative calculation of the weights of each data point based on how far they are from the fitted line.

An example of the correlation between three absorption profiles is shown in Figure 9. The comparison of each pair of DA profiles requires the choice of one of the profiles as a reference profiles which is compared to all the others profiles. The resulting amplitude factors represent a linear estimation of the DA amplitudes relative to the reference DA profile which gets assigned a value of 1.

The result of this approach in the experiment with ten known concentrations (Table 1) is depicted in Figure 10. In this case, the whole set of calibration cells exhibited a non-linear relationship between the DA amplitude and SO\(_2\) path length concentration. This deviation from linearity is particularly stronger with cells of gas concentrations higher than 10 ppm·m. Using all the calibration cells up to 56 ppm·m, it is found that a third-order polynomial model (model B) fits the data better than a quadratic polynomial (model A) (Table 1). The stronger deviation from linearity at high gas concentrations is also evidenced by the good correlation that a quadratic model yields when only two calibration cells are used.

See MATLAB's Help.
Calculate P-L Concentration

\[ DA_{new} = f_h \cdot DA_{high} \quad f_h < 1 \]
\[ DA_{new} = f_l \cdot DA_{low} \quad f_l > 1 \]

\[ C_i = a \cdot \tilde{f}_i^2 + b \cdot \tilde{f}_i \]
\[ \tilde{f}_i = 1 / f_i \]

\[ C_i \cdot f_i = a \frac{1}{f_i} + b \]

\[ C_{new} = a + b \]
Example of Measurements
Procedure for calculation of the SO₂ path-length concentration from raw light spectra data

1. Set parameters of the spectrometer (light correction and fitting ranges) and calculations.
2. Set the calibration
   (a) Read reference (background) and dark (instrument offset) files
   (b) Read spectra and get concentrations of calibration cells
   (c) Calculate and store the differential absorbance of the calibration cells
3. Read files with new measurements
   (a) Read dark and reference files if they are different to the corresponding calibration files
   (b) Open the file with new measurements
4. Loop over the spectra in the new scan file
   (a) Read a single spectrum
   (b) Get the differential absorbance of the new spectrum
   (c) Correlate the differential absorbances of the calibration cells with the new spectrum, and calculate the concentration of SO₂
5. (Optional) Identify and label spikes
6. Plot and save the results