

### **Appendix 3: Mathematical development for the calculation of the peak area and the quantitative calculation of the gas concentration**

The peak areas of each gas ( $A'_i$ ) are therefore corrected by dividing the measured area ( $A_i$ ) by RRSCS ( $\sigma_i$ ) and the instrumental function ( $\xi_i$ ) according to equation (1):

$$A'_i = \left( \frac{A_i}{\sigma_i * \xi_i} \right) \quad (1)$$

Where  $A_i$  = Peak area of gas  $i$  (in arbitrary unity)

$\sigma_i$  = RRSCS of gas  $i$  (without unit)

$\xi_i$  = Instrumental function for gas  $i$  (=1 according to Taquet et al. 2013)

To reduce potential data dispersion, these corrected peak areas are tested with Chauvenet's criteria. This method helps to detect mathematical outliers from the data set according to the following probability law (where  $N$  is the studied measurement number) (Massart et al., 1998) in Eq.(2) :

$$\text{Prob} = 1 - \left( \frac{1}{2N} \right) \quad (2)$$

This law can be related to a maximum deviation away from the mean by using a normal probability law. Thus, all measurements that deviate from the mean by more than the term ( $\tau_{\max} * S_i$ ) can be rejected according to the equation below (3). Each time these Chauvenet's criteria are used, it is necessary to ensure beforehand that the data distribution follows a normal law.

$$\tau_{\max} = \left( \frac{|(A'_i - \bar{A}_i)|_{\max}}{S_i} \right) = \frac{d_{\max}}{S_i} \quad (3)$$

Where  $\tau_{\max}$  = non dimensional maximum deviation factor

$A'_i$  = Peak area of gas  $i$  which has been corrected from the cross-section (in arbitrary unity)

$\bar{A}_i$  = Mean of the dataset of the corrected peak area of gas  $i$  (in arbitrary unity)

$S_i$  = Precision index (Pearson's standard deviation) of the dataset

$d_{\max}$  = Maximum deviation

This statistical method can be used in the geoscience sector (Liu et al., 2017). The relative molar fractions (%) of the gases in the mixture can then be determined by calculating the ratio  $A'_i / \Sigma A'_i$  (Wopenka and Pasteris, 1986; Pasteris et al., 1988).

Thus, each spectrum including an outlier of one of the studied gases identified by the Chauvenet's criteria is removed from the data set. After the processing with Chauvenet's criteria (from 4 to 5 runs) according to the time sub-periods within the baseline period, 7,633 spectra are selected (95.8% of total initial dataset).

Assuming that each molecule in the gas phase is in equilibrium with its respective dissolved species in water, the dissolved gas concentration ( $C_i$ ) was calculated from the Henry's law including mole fractions of each gas (Eq (4)):

$$C_i = P_{\text{Mb}} * \left( \frac{A'_i}{\Sigma(A'_j)} \right) * \frac{1}{K_{\text{Hi}}} * M(\text{gas}) * 1000 \quad (4)$$

Where  $C_i$  = concentration of dissolved gas  $i$  (in mg.L<sup>-1</sup>)

$P_{\text{Mb}}$  = Pressure in the collecting chamber (in atmosphere)

$\left( \frac{A'_i}{\Sigma(A'_j)} \right)$  = Mole fraction of gas  $i$  (without unit)

$K_{\text{Hi}}$  = Henry's constant of gas  $i$  (in L.atm.mol<sup>-1</sup>) at the borehole water temperature

$M(\text{gas})$  = Gas molar mass (in g.mol<sup>-1</sup>)

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