

Calibration

To perform desupersaturation measurements with Raman spectroscopy it was necessary to calibrate the obtained spectra. The above mentioned relation between mass load of a component with the intensity ratio was applied (compare Eq. (3)). Therefor ternary mixtures of both salts and water with known compositions were used. The intensities were represented by the peak areas. The integration boundaries were determined from slope analysis. The boundary was set to the point where the slope changed its sign or the change in slope was lower than 0.0025.

The internal reference material was water. Hence, the intensities of the anion peaks were related to the intensity of the water peak. In Figure S27, calibration functions are shown for both salts solved in water at 25 °C. Ternary solutions were analyzed in order to use calibration samples which have a high content in electrolytic components over a broad concentration range. The solutions are displayed as triangles in the ternary diagram in Figure S27. Two independent solutions at the displayed concentrations were prepared. All calibration functions were forced through origin. Calibration was repeated for other temperatures in the range of 17 to 30 °C. The results showed that the calibration functions displayed in Figure S27 were suitable for the temperature range investigated in this work.

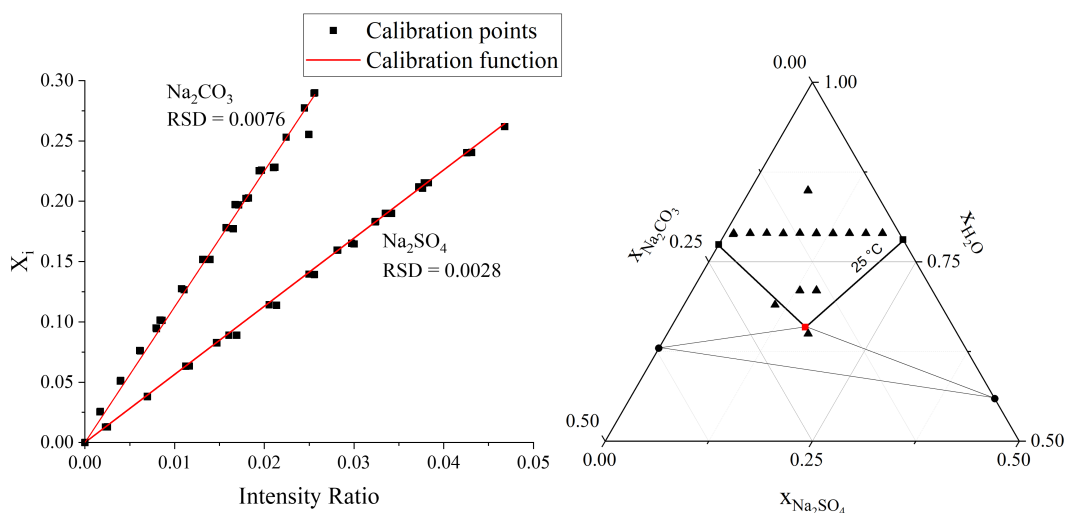


Figure S27: Calibration functions of Na_2SO_4 and Na_2CO_3 related to water at 25 °C. The slopes of the linear functions represent both calibration factors. The residual standard deviations (RSD) for the calibration functions are given. The triangles in the triangle diagram represent the compositions of calibration solutions.

The residual standard deviations (RSD) of both functions from measured points are satisfactorily. The RSD is defined as the square root of the sum of square errors divided

by the degrees of freedom (compare Eq. S1). In the current case the degrees of freedom are the sample number minus one.

$$RSD = \sqrt{\frac{\sum (X_i - \hat{X}_i)^2}{n - 1}} \quad (\text{S1})$$

Thus, the RSD displays the agreement of the calibration function with the calibration standards with the unit of mass load. The resulting linear functions for sodium sulfate and sodium carbonate are displayed in Equations S2 and S3, respectively.

$$X_{\text{Na}_2\text{SO}_4} = 5.65 \cdot \frac{I_{\text{SO}_4^{2-}}}{I_{\text{H}_2\text{O}}} \quad (\text{S2})$$

$$X_{\text{Na}_2\text{CO}_3} = 11.25 \cdot \frac{I_{\text{CO}_3^{2-}}}{I_{\text{H}_2\text{O}}} \quad (\text{S3})$$

With the simple linear regressions ternary compositions during desupersaturation measurements could be determined with an accuracy of $\Delta X_{\text{Na}_2\text{SO}_4} = \pm 0.0028$ and $\Delta X_{\text{Na}_2\text{CO}_3} = \pm 0.0076$.