

Evaluation of some of the main inorganic ions in brine solutions used for sea salt production by flow injection analysis and Fourier-mid infrared spectroscopy



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➤ The production of 'traditional' sea salt is a hand-labour activity which requires the correct management of brine flows coming from the sea which travels through sea pans areas until sodium chloride (NaCl), together with other types of salts (i.e. MgSO₄, MgCl₂ and others), crystallizes.

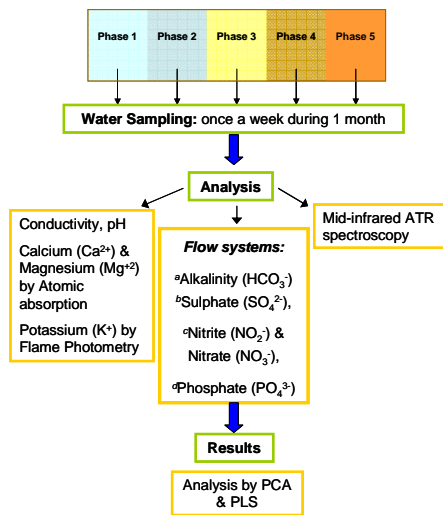
➤ The determination of inorganic constituents in the brine solutions of 'traditional' sea salt, such as SO₄²⁻, HCO₃⁻, Mg²⁺ among others, is of vital importance as the presence of those trace elements in brines will determine the final quality of 'traditional' sea salt.



➤ The main objective of the presented work was to ascertain whether the application of Fourier-mid-infrared-ATR spectroscopy in combination with flow injection analyses are well suitable for the rapid and simple evaluation of brine solutions in terms of different ions like: SO₄²⁻, Mg²⁺, HCO₃⁻, NO₂⁻, NO₃⁻.

Figures a) & b) solar salt works in Portugal c) salt product for commercialization.

Materials and Methods:



Results:

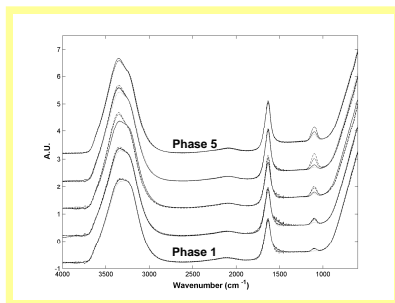


Figure 1. Typical mid-infrared ATR spectral features of brine solutions from different phases of crystallization.

□ Spectra have in common three spectrum bands: the –O–H arising between 3400 to 3200 cm⁻¹ and around 1635 cm⁻¹ and the S=O stretch band at ~ 1100 cm⁻¹.

□ The shift in the –O–H band, in this region could be associated to the variation in the amount of hydrogen bonding caused by sodium chloride (13). Besides of this the increase detected in the intensity of the band at 1635 cm⁻¹ (Figure 1) was associated to the increased of salt ions (5).

□ In an early stage of crystallization (phase 1) the sulphate band is flat, then the band starts to increase with the progress in the crystallization process – phase 5.

Results:

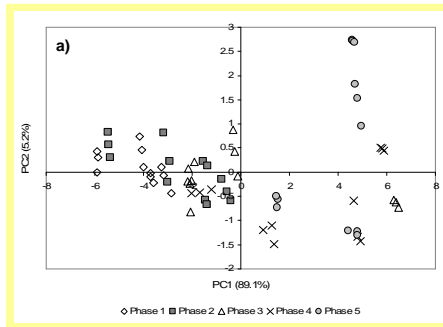
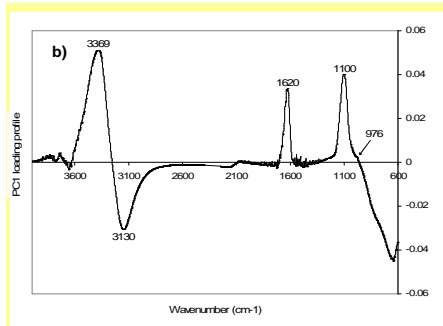
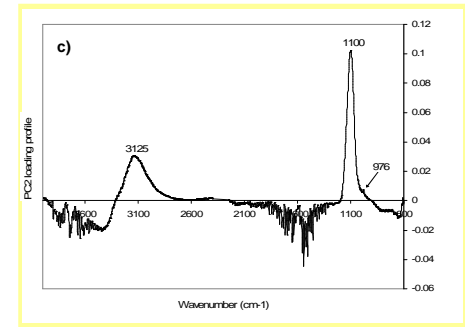


Figure 2. (a) Scatter-plot scores (PC1 vs. PC2) of brine solutions; PC1 (b) and PC2 (c) loading profile plots of brine solutions according phase of crystallization.



- PCA analysis represented in Figure 2a shows a clear separation between the phases 1, 2 and 3 from the 4 and 5.
- The origin of that separation is mainly due to the interaction of the hydrogen bond network with the dissolved ions.
- In the phases 1, 2 and 3 the dissolved ions are less concentrated than in the phases 4 and 5.
- In the brines from phases 4 and 5 exist a significant increase in the ions concentration which cause the increase in the intensities of the –O–H vibrations and the rise of the S=O stretch band at 1100 cm⁻¹ (Figure 2b).
- The loading profile of PC2 confirms the previous observations and also provides evidence of the existence of a contribution of the presence of the MgSO₄ with a small band arising at 976 cm⁻¹ in the positive loading of the PC2 (Figure 2c).

Table 1. PLS regression results

Analytical parameter	R ²	Spectral range (cm ⁻¹)	LV ^b	Pre-processing method ^c
[HPO ₄ ⁻] ppm	0.853	2000-2600	3	SNV+SG(15,2,1)
[NO ₂ ⁻] ppm	0.540	2000-2600	6	SG(15,2,2)
[NO ₃ ⁻] ppm	0.357	4000-2400 & 2250-600	1	none
[HCO ₃ ⁻] ppm	0.804	1300-900	4	SNV+SG(15,2,1)
[SO ₄ ²⁻] ppm	0.873	2000-2600	7	SG(15,2,2)
Ca ²⁺ (ppm)	0.142	2000-2600	1	SNV
Mg ²⁺ (ppm)	0.851	4000-2400 & 2250-600	4	SG(15,2,2)
K ⁺ (ppm)	0.902	4000-2400 & 2250-600	5	SNV

^aLV = latent variables number

^bSNV = standard normal variate, SG = Savitzky-Golay filter (filter size, polynomial order, derivative order)

□ PLS regression results present in Table 1 indicate that for some analytical parameters like K⁺, Mg²⁺, SO₄²⁻, HCO₃⁻ and HPO₄⁻ good correlations were established between the reference analytical procedure and the spectral data.

□ For the improvement of regression models, specially for parameters like Ca²⁺ and NO₂⁻ and NO₃⁻, an increase in the samples number will be necessary.

□ The application of mid-infrared spectroscopy in combination with flow systems opens a new possibility for the analysis of aqueous matrices in a rapid and simple way.

References:

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