

Near infrared spectroscopy to evaluate metal ion speciation in water

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Introduction

The environmental impact and toxicity of metal ions in natural water sources can be evaluated only through the knowledge of the reactions that these ions give rise to. Metals are usually present in aqueous solutions as cations, surrounded by a number of water molecules depending on their coordination ($M(H_2O)_n^{z+}$; where “M” is a generic cation with charge $z+$). Inorganic ligands (Cl^- , F^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , $C_2O_4^{2-}$), and monomeric (polycarboxylic acids) or polymeric organic ligands derived from the decomposition of organic material (humic and fulvic acids), can be found in surface and deep natural waters. The presence of such ligands can cause the formation of soluble complexes or lead to precipitation reactions. Several parameters determine whether precipitation reactions will occur, such as pH and relative concentrations of the metal ion and the ligands.¹ Given the complexity of real systems, the study of possible reactions must be first directed towards subsystems that are less difficult to analyse. At the typical pH conditions of natural water sources, the formation of hydroxocomplexes and carbonate and bicarbonate complexes are some of the most favored reactions. Analysing these reactions is the first step in studying the speciation of a metal ion in a real solution. The study of such subsystems is thus necessary for the production of a database² useful to speciation, defined as the qualitative and quantitative determination of species at the equilibrium, among which the examined metal ion is distributed.

The study of metal ions in aqueous solutions by near infrared (NIR) spectroscopy requires knowledge of the response of each ion in the corresponding spectral region. It has been well established that cations and anions can modify the water matrix through the formation of hydrogen bonds, the formation of ion pairs and the onset of charge-dipole interactions between ions and water molecules. Unfortunately, metal ions don't exhibit absorption in the NIR region and have to be interpreted from influences on water vibrational modes. Previous studies have shown the possibility of distinguishing between metal ions at very low pH values using NIR spectroscopy.^{3,4}

The aim of this work was to verify the utility of NIR spectroscopy in highlighting the changes that occur in aqueous solutions with two different cations (Zn^{2+} , Pb^{2+}) in a wide range of pH conditions, under ambient atmosphere. In particular, this study sought evidence for the formation of i) ion pairs, ii) hydrolysis complexes, and iii) complexes with bicarbonate ion always present in solutions in contact with air. On the basis of NIR spectroscopic principles and theory, this aim can be indirectly reached only observing the spectral variations occurring in water absorption bands (combination bands and overtones). Zn^{2+} and Pb^{2+} were chosen to be studied because of their environmental impact and toxicity, and because these ions undergo hydrolysis reactions at increasing pH values.

Materials and Methods

Samples

Zinc powder (Carlo Erba, Italy) and $Pb(NO_3)_2$ (Merck, Germany) were used to prepare Zn^{2+} and Pb^{2+} solutions (ionic medium: 0.2 M (Na)NO₃ (Merck, Germany); final concentration of the cation: 50 mM). Zn^{2+} and Pb^{2+} ion solutions were prepared under ambient atmosphere, using 0.2 M (Na)NO₃ as an ionic medium. Decreasing pH values were obtained by adding to the initial solutions, prepared at pH 5 or 6, the known volumes of cation solutions with identical compositions but lower pH values. This was obtained by the addition of HNO₃ solutions at different concentrations (10^{-1} , 10^{-3} N). pH measurements were performed with a WTW pH 340th (WTW, Weilheim, Germany) pH meter. pH values of Zn^{2+} solutions ranged from 2 to 6, and from 2 to 5 for Pb^{2+} solutions, in order to avoid the precipitation of metal hydroxide. pH values of solutions containing only 0.2 M (Na)NO₃ ranged from 2 to 6.

Near infrared spectroscopy

Fourier transform (FT) NIR spectra of solutions containing 0.2 M (Na)NO₃ (46 samples), Zn^{2+} (51 samples) and Pb^{2+} (36 samples), were acquired in transmittance mode (optical path 0.2 mm, 32 scans, resolution 8 cm⁻¹, three replicates) with a NIRFlex N-500 spectrometer (BUCHI Italy, Assago, Milan). The spectra were

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collected in the wavenumber range from 4000–10000 cm^{-1} using NIRWare Operator version 1.2 (BUCHI Italy, Assago, Milan) at a controlled temperature ($40^\circ\text{C} \pm 1^\circ\text{C}$).

Data processing

The collected spectra, averaged and mean centred, were processed using the Unscrambler version 9.2 software (Camo Inc., Oslo, Norway) by principal component analysis (PCA) after the application of standard normal variate (SNV) algorithm and second derivative processing (Savitzky-Golay, 8 points, polynomial order = 2) as pretreatments. Partial Least Squares (PLS) analysis was then performed to develop a model to predict the pH of the solutions by the spectral data. PLS was applied after pretreating samples with SNV, smoothing by moving average (5 points) and mean centring, and independent datasets were used to validate the PLS model (Table 1).

Results and discussion

This NIR study of the speciation of metal ions began by verifying the sensitivity for detecting variations in the water matrix. Under the specific experimental conditions, three phenomena occurred in the solutions of Zn^{2+} and Pb^{2+} in 0.2 M (Na)NO₃. 1) Ion pairs formed between the studied cations and nitrate anions: a phenomenon that may occur by a perturbation of the hydration shell of cations.^{5,6} 2) Hydroxocomplexes formed, including PbOH^+ , $\text{Pb}_4(\text{OH})_4^{4+}$, $\text{Pb}_6(\text{OH})_8^{4+}$ for Pb^{2+} and ZnOH^+ , $\text{Zn}(\text{OH})_2$ for Zn^{2+} , as have previously been reported.^{7,8} 3) Bicarbonate ion complexes formed, like ZnHCO_3^+ and PbHCO_3^+ , with the simplest stoichiometric composition.^{9,10} By modifying the water matrix and its typical vibrational modes, these phenomena and reactions reveal the presence of cations in solution.³ The different nature, in terms of hydration and structure, of the ions and the different stoichiometries of the reactions are the basis to distinguish among them.

PCA was performed on solutions with pH values ranging from 2 to 3 and distinguished the three solution sets by shifts in the water band centred at 5248 cm^{-1} (Figures 1 and 2). Concentration was not relevant over pH values 2 to 3 because of the complexes; shifts in the water band should occur by the pairing a metal ion with a nitrate anion, or by a different hydration of the analysed ions.

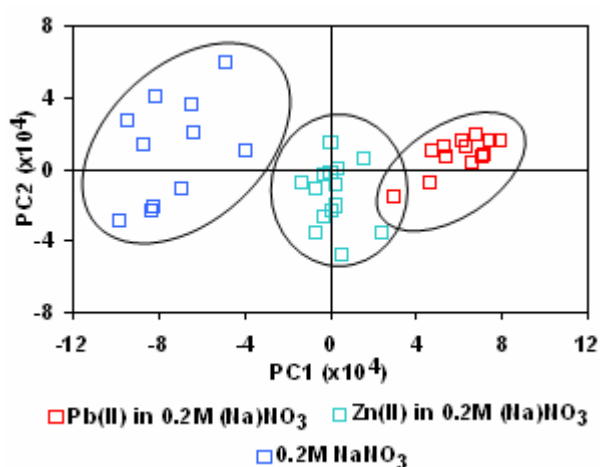


Figure 1. Scores plot obtained from the PCA analysis performed on 38 samples (11 of 0.2 M (Na)NO₃; 14 of Zn^{2+} in 0.2 M (Na)NO₃ and 13 of Pb^{2+} in 0.2 M (Na)NO₃).

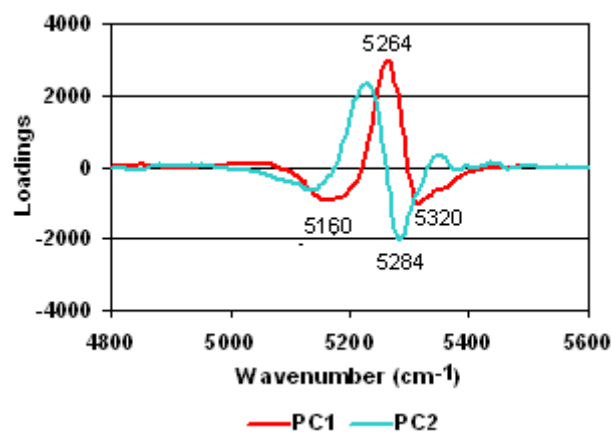


Figure 2. Loadings plot on PC1 and PC2 obtained from the PCA analysis performed on 38 samples in the range from 4800 to 5600 cm^{-1} .

Differences between the solutions were appreciable along the first principal component (PC1), which explained 78% of the total variance. Solutions containing Pb^{2+} in 0.2 M (Na)NO₃ and solutions containing only 0.2 M NaNO₃ were positioned respectively on the positive and the negative sides of the PC1 axis, and solutions containing Zn^{2+} in 0.2 M (Na)NO₃ were positioned at PC1 values near zero. PC2 explained a further 13% of the total variance, this group of samples mostly showed negative values. From these data alone it is difficult to attribute the observed signals to a physical state of each ion in solution. However, the observed sample separation could be considered the first step towards understanding the contribution that NIR spectroscopy may make in studying metal ions in solution.

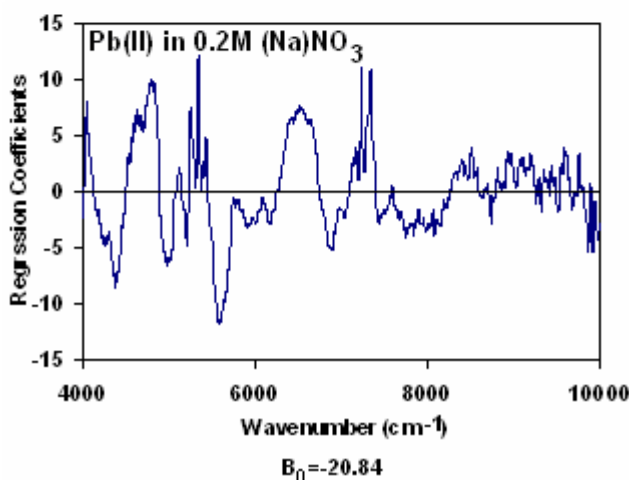
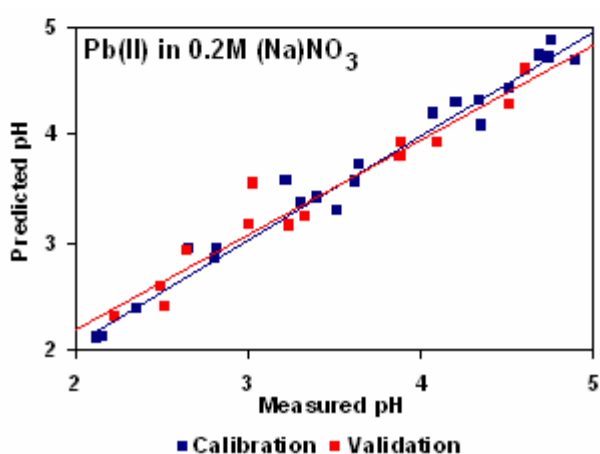
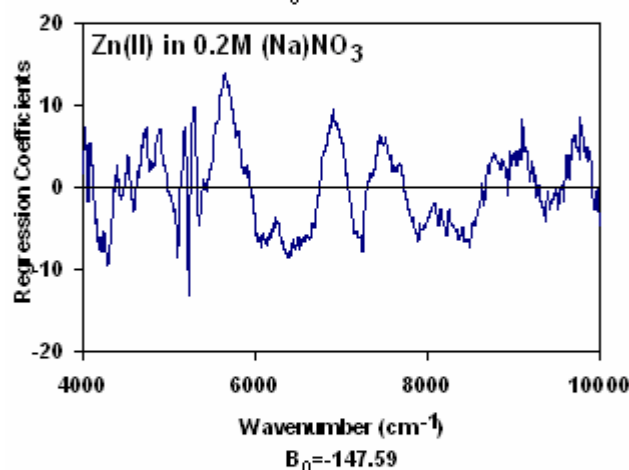
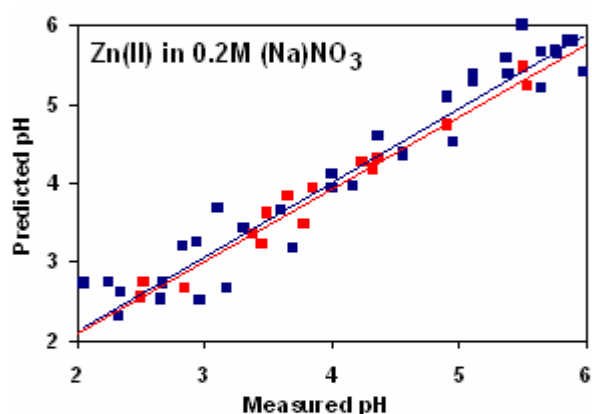
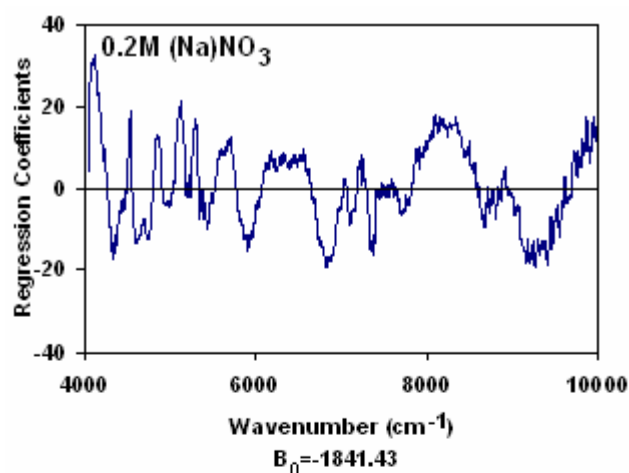
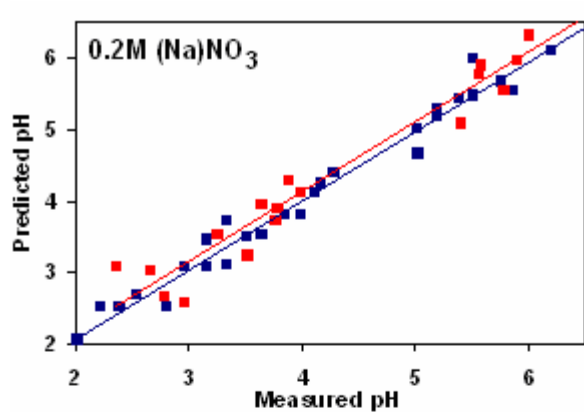


Figure 3. PLS calibration models for predicting pH in solutions of 0.2 M (Na)NO₃, Zn²⁺ in 0.2 M (Na)NO₃, Pb²⁺ in 0.2 M (Na)NO₃.

Figure 4. Regression coefficients for calibration models to predict pH in solutions of 0.2 M (Na)NO₃, Zn²⁺ in 0.2 M (Na)NO₃, Pb²⁺ in 0.2 M (Na)NO₃.

PLS analysis was performed 1) to build a prediction model for pH of the studied solutions, and 2) to verify the sensitivity of NIR spectroscopy for detecting variations in an aqueous cationic solution when the pH is changed. Predicted pH vs. measured pH values are reported in Figure 3. Regression coefficients calculated across the whole NIR range are shown in Figure 4. Note that it was possible to identify regression coefficients that could describe predicted pH as equal to $B_0 + B_1x_1 + B_2x_2 + \dots + B_Kx_K$, where $B_0, B_1, B_2, \dots, B_K$ are the regression coefficients and $x_1, x_2, \dots, x_K$ are the selected wavenumbers. Statistics for the PLS regression models (Table 1) are reported in terms of: i) number of samples used for calibration and validation; ii) number of PCs; iii) coefficient of determination in calibration (R^2_{CAL}); iv) standard error of calibration (SEC); v) coefficient of determination in validation (R^2_{VAL}) determined by test set validation; vi) standard error of prediction (SEP); vii) ratio of performance to deviation (RPD) calculated as SD_{pH}/SEP , where SD_{pH} is the standard deviation of pH values used in the validation test set.

Table 1. Statistical parameters for PLS models.

Parameters	0.2 M (Na)NO ₃	Zn ²⁺ in 0.2 M (Na)NO ₃	Pb ²⁺ in 0.2 M (Na)NO ₃
No. of samples for Calibration	28	35	23
No. of samples for Validation	18	16	13
Principal components	11	10	8
R ² _{CAL}	0.974	0.936	0.971
SEC	0.206	0.330	0.162
R ² _{VAL}	0.947	0.977	0.938
SEP	0.304	0.177	0.200
RPD	4.30	5.97	3.93

Differences among regression coefficients (Figure 4) suggest that water interactions changed with pH: such changes can be ascribed to the different compositions of the studied solutions. In contrast, a relationship was not evident between the regression coefficients obtained for the 0.2 M (Na)NO₃ solutions, or for the solutions containing Pb²⁺ and Zn²⁺. These preliminary results suggest that it might not be possible to distinguish among different phenomena in a simple way, so this experimental paper should be considered the starting point for more thorough investigations.

Conclusion

The information obtained in this work demonstrated the NIR spectroscopic sensitivity for the detection of changes in aqueous ionic solutions. In particular, NIR spectroscopy can be used to distinguish different ionic compositions, as well as pH changes and associated phenomena. Nevertheless, an exhaustive interpretation of the obtained results is still a goal to be achieved. This first paper should be considered the starting point for more thorough investigations. Further experiments will address the identification of possible phenomena occurring in aqueous solutions containing cations and anions, such as the formation of ion pairs, hydrolysis complexes and complexes with bicarbonate ions. Future tests will be performed at well defined pH values, and by bubbling ionic solutions with an inert gas to eliminate the interference of bicarbonate. The interpretation of the results in terms of radius, hydration number, charge and density charge of the analysed ions would also be an ambitious aim of future works.

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