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Optical Raman probe of chlorine determination in waste water

T. Kauffmann, K. Ben Mabrouk and M.D. Fontana

Laboratoire Matériaux Optiques, Photonique et Systèmes
Université de Lorraine and Supélec, 57070 Metz, FRANCE
email: thomas.kauffmann@metz.supelec.fr

Summary

We propose to detect by Raman spectrometry the presence of chlorid anion in mixtures of salted solutions. Here is shown how Cl^- influence the OH stretching band of the water spectrum and how its concentration is determined using chemometrics methods applied on Raman spectra recorded on mixtures in few seconds.

Introduction

Chlorine solutions are widely used for disinfection of drinking water or swimming pools as well as in industry and may have serious consequences on health and environment. It is therefore essential to control and measure its concentration quickly and safely. Here we propose the Raman spectroscopy as an optical method for water quality control allowing in-situ, fast, contactless or immersion measurement of chlorides.

Aqueous chlorine solutions made from NaCl or CaCl_2 are often used for winter viability and are an important source of environmental pollution due to overdose and misuse. We recently propose a Raman probe able to measure the residual NaCl concentration on the pavement [1]. The Raman spectrum does not exhibit specific lines characterizing the presence of NaCl but the broad OH band between 2700 and 4000 cm^{-1} is affected by the chloride anion [2]. A relevant concentration calibration can therefore be obtained using the integrated intensity of the band [3].

The problem is more complicated to be resolved when NaCl is dissolved in water with other salts in a mixture. This is the case in the environment with nitrates, sulfates or phosphates which are frequently used in agriculture as fertilizers and are increasingly present in ground waters, basins or rivers [4]. These salts can affect the OH stretching band as shown in Fig 1, and therefore impede the determination of the chloride anion concentration. Thus, from the calibration using the integrated intensity of the OH band, NaCl concentration is erroneously found to be equal to 0.6g/l in a mixture composed of 30g/l of NaCl (i.e. 0.51M of Cl^-) added with 50g/l of ammonium salts.

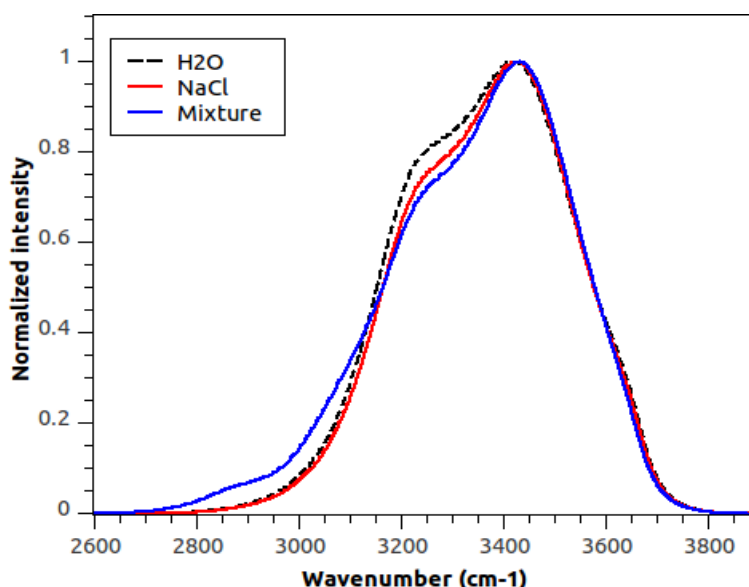


Fig 1. OH stretching band for a pure NaCl solution (in red) and a salt mixture (in blue)

Discussion

One solution consists in using chemometric methods based on statistical studies in order to extract the most information of a spectrum [5]. Here is applied a Principal Component Analysis (PCA) which uses an orthogonal transformation in order to reduce the number of initial variables and turn them into uncorrelated variables called principal components (PC). These PC are ranked in order of largest possible variance. A linear regression using the first PC which represents the best the Cl⁻ concentration effect can then be done on a set of NaCl spectra at different Cl⁻ concentration from 0 up to 3.42M to get a calibration.

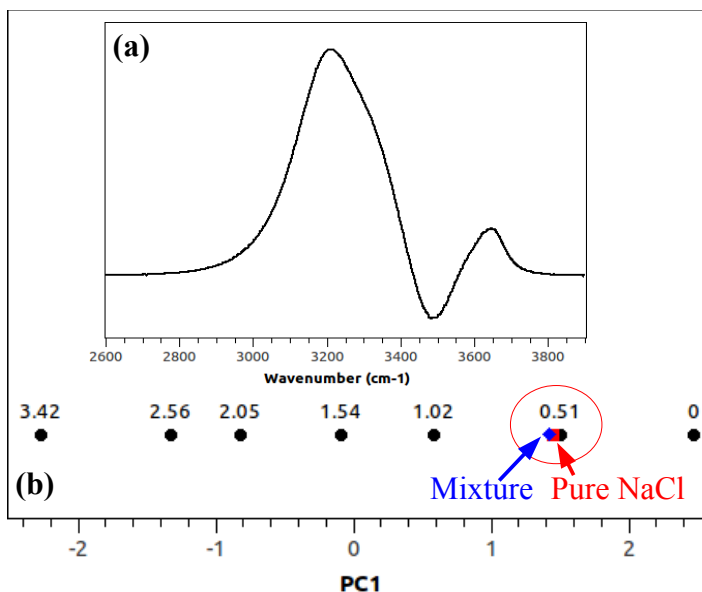


Fig 2. (a) First component and (b) scores distribution according to PC₁. Labels indicate the Cl⁻ concentration in mol/l (M).

Principal component regression (PCR) gives us a good calibration ($R^2 = 0.9852$) and better results than the integrated intensity method. We predict now using the PCR method a Cl⁻ concentration of 0.54M (31.5g/l) instead of 0.51M for a pure 30g/l NaCl solution and a concentration of 0.55M (32.2g/l) for the mixture solution. So with the PCA method the Cl⁻ concentration found for the mixture is now very close to the real chloride concentration of 0.51M (30g/l) despite the presence of ammonium salts as shown in Fig 2.

Conclusions

Raman spectroscopy can be a good way to detect and to measure quickly the concentration of chlorides in aqueous solution. The use of chemometric tools can be very useful for the measurement of different salts in hostile environments with many disturbances (mixtures, temperature...).

We work to implement methods on field (basins, rivers) for the simultaneous detection and quantification of several ion in solution (chloride, nitrate, nitrite, sulfate, phosphate), with the advantages of the Raman spectroscopy : in-situ, fast (few seconds), remotely or not and reliable measurement.

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