



Two-dimensional correlation analysis to study variation of near-infrared water absorption bands in the presence of inorganic acids



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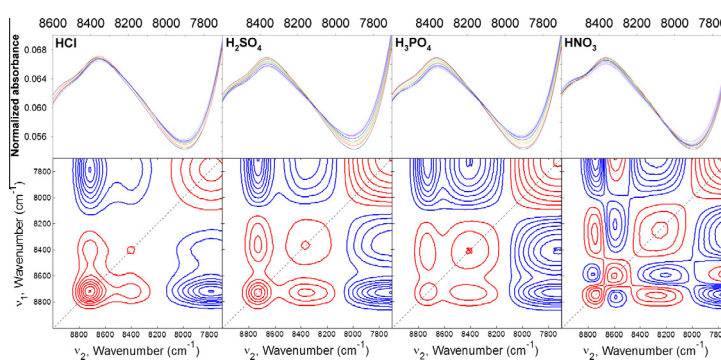
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HIGHLIGHTS

- NIR water band was varied by presence HCl, H₂SO₄, H₃PO₄, HNO₃ was investigated by 2D-COS.
- The variation was due to interaction of dissociated ions with water vibration.
- 2D COS revealed that individual acids differently influenced water vibration.

GRAPHICAL ABSTRACT



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ABSTRACT

Two-dimensional (2D) correlation analysis has been utilized to investigate NIR water bands perturbed by the presence of four different inorganic acids individually: HCl, H₂SO₄, H₃PO₄, and HNO₃. The observed spectral variation in the 9000–7700 cm⁻¹ range was mainly due to interaction of dissociated H₃O⁺ and corresponding anions with the vibration of water in a hydrogen bonding network. 2D correlation analysis of NIR spectra acquired from sample solutions (concentration range: 0.2–1.0 M) showed that individual acids differently influenced water vibration. In addition, unforeseen spectral variations under the water band that were difficult to identify with corresponding raw NIR spectra were clearly observed. Based on the asynchronous correlation analysis, three underlying individual variations occurred for HCl under the 8718 cm⁻¹ band. Only two asynchronous correlations were observed for H₂SO₄ and H₃PO₄. The 2D correlation features of HNO₃ were distinctly different from those of the other three acids due to an additional spectral feature caused by direct absorption by NO₃⁻. The dissimilar influence of the selected acids on water vibration was confirmed by NIR spectroscopy combined with 2D correlation analysis. Partial least squares (PLS) loadings from each case were compared to examine the difference in weights that were constructed to follow the corresponding concentration changes.

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1. Introduction

Near-infrared (NIR) spectroscopy has been demonstrated as a viable analytical method to measure concentrations of components in diverse wafer etchant solutions [1,2] composed of an oxidizing

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agent (H₂O₂) and acids. Usually, strong inorganic acids such as HCl completely dissociate into hydronium ions (H₃O⁺) and a corresponding anion in an aqueous solution. The dissociated species directly absorb NIR radiation and/or interact with water hydrogen bonding networks to alter the NIR spectral features of water. In our previous publications, HCl and HF concentrations were measured in etchant solutions by recognizing water bands [1–3] rather than direct NIR absorption [4–6]. The altered water spectral features

were found to correlate with corresponding concentration changes using multivariate calibration methods such as partial least squares (PLS).

Because water spectral features vary without a distinct signature, the component-specificity and robustness of a PLS model are of interest. An in-depth investigation on the effects of dissolved inorganic acids on the NIR spectral features of water has not been performed even though perturbed water bands are a valuable source for determining concentration. More profound investigations of water band variation are necessary to validate the selectivity (component-specificity) of a PLS model.

This publication investigated the variation in NIR water bands with dissolved inorganic acids using generalized two-dimensional (2D) correlation analysis. For this purpose, four different inorganic acids (HCl, H₂SO₄, H₃PO₄, and HNO₃) were selected, and the NIR spectra of acid solutions were collected within a concentration range of 0.2–1.0 M. 2D correlation analysis was then performed to investigate the water bands perturbed by each acid, and the dissimilarity in perturbations was examined. A cross-validated PLS model was built using each spectral dataset, and corresponding PLS loadings were compared to identify the difference in weights utilized to describe concentration changes.

2. Experimental

High purity HCl, H₂SO₄, H₃PO₄, and HNO₃ were purchased from a common supplier. For each acid, nine solutions with concentrations ranging from 0.2 to 1.0 M (increment intervals of 0.1 M) were prepared, and NIR spectra (resolution: 8 cm⁻¹) were collected using an ABB Bomem MB-160 FT-NIR spectrometer (Quebec City, Quebec, Canada) equipped with a tungsten-halogen source and InGaAs detector. The samples were transferred into a glass vial inserted into a heated metal vial holder that could control temperature with a precision of ±0.1 °C. The temperature of all samples was maintained at 25.0 °C during spectral collection. Air was used as background for absorbance spectra. All spectral pre-processing and multivariate analyses, including baseline correction, normalization, 2D correlation analysis, and PLS, were performed using MATLAB Version 7.0 (Math Works Inc., MA, USA).

3. Results and discussion

3.1. NIR spectral features of HCl, H₂SO₄, H₃PO₄, and HNO₃ solutions

Fig. 1(a–d) shows normalized NIR spectra (9000–7700 cm⁻¹ range) of HCl, H₂SO₄, H₃PO₄, and HNO₃, respectively, within a concentration range of 0.2–1.0 M. For normalization, the baselines of raw spectra were vertically corrected and zeroed at 9000 cm⁻¹. The baseline-corrected spectra were then divided by the corresponding integrated areas calculated in the 9000–7700 cm⁻¹ range [7,8]. For comparison, the NIR spectrum of pure water, corresponding to the second overtone of the –OH vibration, was included in each plot. For better analysis, spectral variation in the 8600–7700 cm⁻¹ range was also highlighted in each figure. The overall spectral features are similar to those of water for each case, and minute spectral variation occurred around the water band according to the change in acid concentration. This indicates that the four acids do not have distinct absorption features. To examine spectral variation in detail, difference spectra were obtained by subtracting individual acid spectra from a pure water spectrum. Difference spectra are displayed for HCl, H₂SO₄, H₃PO₄, and HNO₃ in Fig. 1(e–h), respectively.

HCl completely dissociates into H₃O⁺ and Cl⁻. Since Cl⁻ does not absorb NIR radiation, the observed spectral variation originated from the presence of generated H₃O⁺ and Cl⁻. These ions caused

displacement of water molecules and/or perturbation of the water band, resulting in variation of water spectral features. As shown, two different types of spectral variation are noticeable with changes in HCl concentration. The magnitude of water absorption decreased with increased HCl concentration in the 9000–8300 cm⁻¹ range, while it increased simultaneously in the 8200–7700 cm⁻¹ range. The positive and negative scales in the difference spectra indicate decreased and increased water absorption, respectively. The decrease in absorption in the 9000–8300 cm⁻¹ range is due to displacement of water molecules caused by H₃O⁺ and Cl⁻. As previously studied, water displacement always occurs when foreign components are added into pure water [8–10]. The increase of water absorption in the 8200–7700 cm⁻¹ range originated from broadening of the water band. Absorption features in this range correspond to the left edge of the highly absorbing second overtone water band centered at 6800 cm⁻¹. When charged species are present in water, they interact with the water hydrogen bonding network and increase diversity in water vibration. This results in band broadening, as indicated in previous publications [8,10]. Therefore, increased absorption is due to the widened bandwidth of the second overtone water band caused by greater interaction with dissociated species.

Spectral variation with H₂SO₄ is generally similar to that with HCl, although the spectral difference around 8400 cm⁻¹ is more significant and the magnitude of spectral variation in the range of 8200–7700 cm⁻¹ is greater for H₂SO₄. Spectral variations around 8700 and 8400 cm⁻¹ become less and more significant, respectively, for H₃PO₄. The variation occurring around 8400 cm⁻¹ is likely due to perturbed water vibration caused by large ions such as HSO₄⁻ and H₂PO₄⁻, which are the predominant anion species in H₂SO₄ and H₃PO₄ solutions, respectively. In contrast, the spectral variation around 8400 cm⁻¹ is minimal for HCl. The second acid dissociation constant (*K*_{a2}) of H₂SO₄ is 1.03 × 10⁻², indicating a considerable amount of SO₄²⁻ (10.7–25.4% relative to that of HSO₄⁻) in the same matrix, and SO₄²⁻ also participates in the interaction with water molecules. The second (*K*_{a2}) and third acid dissociation constants (*K*_{a3}) of H₃PO₄ are 6.34 × 10⁻⁸ and 4.22 × 10⁻¹³, respectively, indicating that the concentrations of HPO₄²⁻ (7.48 × 10⁻⁵ ~ 0.135% relative to that of H₂PO₄⁻) and PO₄³⁻ are very low, and their influences on water spectral features are insignificant. Due to differences in the structure, size, and charge of dissociated anion species from H₂SO₄ and H₃PO₄, their perturbations of water vibration are dissimilar, resulting in different spectral variations.

When two mono-protic acids (HCl and HNO₃) are compared, their spectral variations are clearly different. The spectral difference around 8300 cm⁻¹ for HNO₃ is due to the presence of NO₃⁻, a larger anion than Cl⁻. Another noticeable feature in the HNO₃ spectra is increased absorption at 8600 cm⁻¹ due to the direct absorption of NO₃⁻ (second overtone of NO stretching) [7,11]. The dissociated anions from H₂SO₄ and H₃PO₄ do not absorb NIR radiation in this range. Overall, NIR spectral features differ with varying HCl, H₂SO₄, H₃PO₄, and HNO₃ concentrations.

3.2. Two-dimensional (2D) correlation analysis to examine water band variation with changes in HCl, HNO₃, H₂SO₄, and H₃PO₄ concentrations

Generalized 2D correlation analysis is helpful for identifying unforeseen and minute spectral variation that is difficult to recognize in original raw spectra [12]. 2D correlation analysis can effectively capture spectral feature changes in response to an applied perturbation, such as increases/decreases in intensity and shifted band position. Nine NIR spectra in the concentration range from 0.2 to 1.0 M for each acid were used for 2D correlation analysis. The applied perturbation was increased interaction with water

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