

1 **Title Page**

2 *Supplementary material*

3

4 **Real-time analysis and prediction method of ion concentration**
5 **using the effect of O–H stretching bands in aqueous solutions**
6 **based on ATR-FTIR spectroscopy**

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3 **Table S1. Preparation parameters for mixed solution samples.**

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5 **Figure S1. Differences in the absorbance of the O–H stretching band at $3,300\text{ cm}^{-1}$ in LiCl + NaCl**
6 **(LiOH + NaOH+ HCl) solutions based on two cations (Li^+ , Na^+) molarities.**

7 **Figure S2. ATR-FTIR modified absorbance and deconvolution peaks based on Li^+ and Na^+**
8 **molarities. a. Li^+ 1 M + Na^+ 1 M, b. Li^+ 1 M + Na^+ 2 M, c. Li^+ 2 M + Na^+ 1 M, d. Li^+ 2 M + Na^+ 2**
9 **M.**

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1 < PLS regression analysis >

2 The data obtained from Tests 4 and 5 for LiCl (LiOH + HCl) and NaCl (NaOH + HCl) were used to
3 perform PLS regression analysis. The analysis was conducted using MATLAB version 24.1.0.2603908
4 (R2024a) Release Update 3 (The MathWorks, Natick). The concentrations of Li⁺ and Na⁺ in the
5 prepared samples were set as the independent variables X1 and X2, respectively, and normalized. The
6 ATR-FTIR absorbance values corresponding to the concentrations were set as the dependent variables
7 Y1 (Li⁺) and Y2 (Na⁺). The following PLS model was derived through PLS regression analysis:

$$8 \begin{bmatrix} Y1 \\ Y2 \end{bmatrix} = \begin{bmatrix} -0.4995 \\ -0.4937 \end{bmatrix} \cdot \begin{bmatrix} X1 \\ X2 \end{bmatrix}.$$

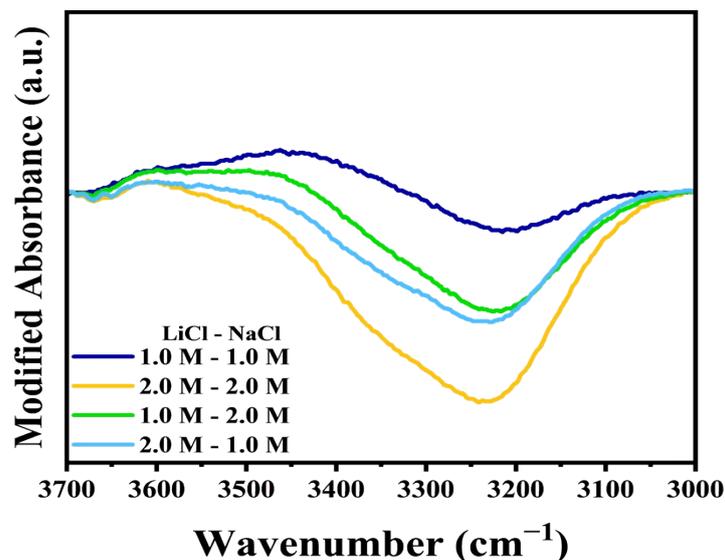
9 To validate the model, we examined the mean squared error (MSE) and the coefficient of determination
10 (R²) between the predicted and actual values. The results showed excellent accuracy with an MSE and
11 R² of 0.0102 and 0.9864, respectively. However, this PLS model has limitations in analyzing the
12 concentrations of unknown solutions wherein Li⁺ and Na⁺ ions are mixed. Therefore, we experimentally
13 verified whether the absorbance differed with the concentrations of each cation in solutions where both
14 ions were mixed, as described below.

15 <Mixed Solution Experiment>

16 To measure the absorbance with respect to the concentration of a solution containing the two ions, ATR-
17 FTIR absorbance measurements were performed. Table S1 lists the concentrations of the solutes. The
18 results are shown in Fig. S1. The absorbance change linearly with a negative slope, and it decreases as
19 the concentration of Li⁺ and Na⁺ in the mixed solution increases. Additionally, the ATR-FTIR
20 absorbance consistently decreases as the concentration of Na⁺ increases from 1.0 M to 2.0 M,
21 irrespective of the concentration of Li⁺. Furthermore, a small absorbance difference of 0.0022 is
22 observed even when the total cation concentration is 3.0 M, such as when the concentrations of Li⁺ and
23 Na⁺ are 1.0 M and 2.0 M, respectively, and 2.0 M and 1.0 M, respectively.

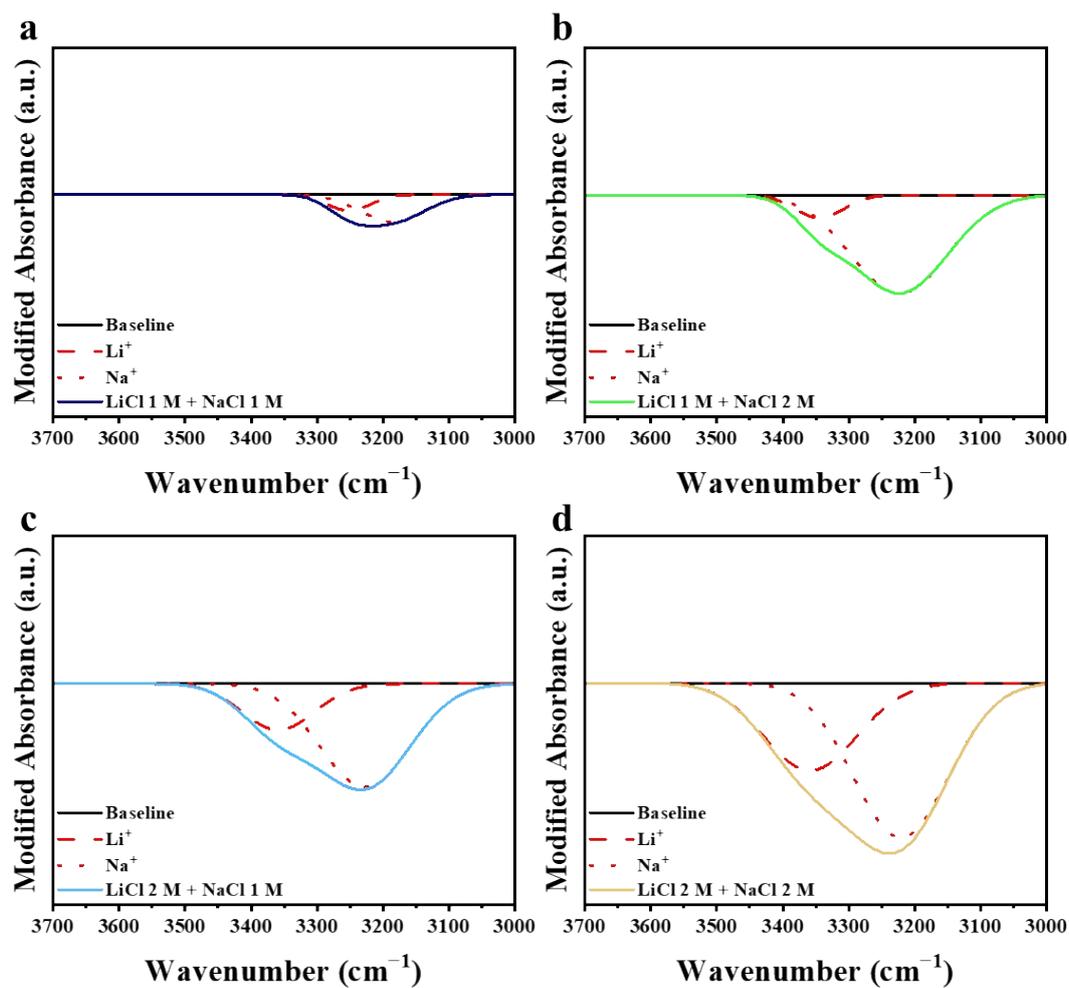
24
25 **Table S1.** Preparation parameters for mixed solution samples.

Test	Solutions	Solutes	Molarity (M)				
6	LiCl + NaCl	LiOH	0.5	1	1	2	2
		NaOH	0.5	1	2	1	2
		HCl	3	3	3	3	3



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2 **Fig. S1** Differences in the absorbance of the O–H stretching band at 3,300 cm^{-1} in LiCl + NaCl
3 (LiOH + NaOH+ HCl) solutions based on two cations (Li^+ , Na^+) molarities.
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5 The ATR-FTIR absorbance of a solution containing a mixture of two types of cations was measured
6 to separate the overlapping peaks in the waveband near the 3,300 cm^{-1} region into two peaks. We
7 utilized a peak analysis method called Fourier self-deconvolution, which enables the separation of the
8 absorbance peaks of mixed ions into their individual components.¹ Fourier self-deconvolution is a
9 mathematical technique used in spectroscopy to increase the resolution of a spectrum. The method is
10 primarily used to separate overlapping peaks for enabling clearer analysis. Given the importance of
11 selecting appropriate filter parameters, as an improper choice can lead to distorted results, we carefully
12 selected two wavebands near the 3,300 cm^{-1} region that correlated with the concentration changes of
13 the two ions. This was possible because the two ions (Li^+ , Na^+) have different hydrogen bonding states
14 with water molecules. As shown in Fig. S2, Li^+ and Na^+ were identified with an absorbance peaks at
15 approximately 3,300 cm^{-1} and 3,200 cm^{-1} , respectively.² The absorbance peaks of the two ions
16 interfered with each other, complicating the interpretation of the separation. However, they were
17 correlated, with the peak intensity increasing proportionally with the concentration of each ion. This
18 result demonstrates the potential application of the proposed method in multivariate analyses.



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Fig. S2 ATR-FTIR modified absorbance and deconvolution peaks based on Li⁺ and Na⁺ molarities.

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a. Li⁺ 1 M + Na⁺ 1 M, **b.** Li⁺ 1 M + Na⁺ 2 M, **c.** Li⁺ 2 M + Na⁺ 1 M, **d.** Li⁺ 2 M + Na⁺ 2 M.

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