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Quantitative Sensing of Na^+ and K^+ Ions in Aqueous Solutions Using Multi-wavelength NIR Spectroscopy

Ryotaro Kawashima,[1] Motohiro Kasuya,[2] Miyu Nakazato,[3] Jun Hirayama,[4]
Masamichi Nogawa,[3] Shinobu Tanaka,[5] and Ikuto Suzuki[3]*

[1]Department of Clinical Engineering, Nagoya University Hospital,
65 Tsurumai-cho, Showa-ku, Nagoya 466-8560, Japan
[2]Division of Production of System Sciences, Graduate School of Sustainable Systems Science, Komatsu University,
Nu 1-3 Shicho-machi, Komatsu, Ishikawa 923-8511, Japan
[3]Department of Clinical Engineering, Faculty of Health Sciences, Komatsu University,
He 14-1 Mukai-motoori-machi, Komatsu, Ishikawa 923-0961, Japan
[4]Faculty of Education, Bunkyo University, 3337 Minami-Ogishima, Koshigaya, Saitama 343-8511, Japan
[5]Institute of Transdisciplinary Sciences for Innovation, Faculty of Transdisciplinary Sciences for Innovation,
Kanazawa University, Kakuma-machi, Kanazawa 920-1192 Japan

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Investigating sweat component concentrations is important for managing electrolyte balance and water content in the body, monitoring hydration and heat stress, and preventing dehydration. Predicting rehydration timing for regulating body temperature and preventing dehydration is particularly challenging because it depends on the individual's health and exercise status, which affects the amount and composition of sweat. Consequently, there is a demand for a simple analytical method using a portable device for practical applications. In this study, sodium and potassium concentrations were evaluated in aqueous solutions using multi-wavelength NIR spectroscopy. The number of wavelengths necessary for accurate analysis was also verified using multiple regression analysis. The concentrations of aqueous sodium and potassium electrolytes were evaluated by multiple regression analysis using the differential absorbance of the samples obtained using a NIR spectrometer. By using four and five wavelengths for each of the two electrolytes, the accuracy of the correlation coefficient between the optically evaluated concentration and the concentration measured using a commercial ion meter exceeded 0.9995. A multi-wavelength NIR spectroscopic method was developed for the optical evaluation of electrolyte concentrations in aqueous solution. The concentration evaluation was achieved using two wavelengths, leading to the development of a simple device for measuring sweat components.

1. Introduction

Sweat is a complex biofluid consisting primarily of water, sodium ions, chloride ions, potassium ions, glucose, and lactic acid.(1) The loss of electrolytes and water through sweating is

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*Corresponding author: e-mail: ikuto.suzuki@komatsu-u.ac.jp
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directly related to the electrolyte balance in the body, affecting dehydration, exercise capacity,(2,3) and body temperature regulation.(4) Compared with blood collection, sweat collection is less difficult because it can be collected noninvasively and without restrictions on collection sites. Therefore, disease diagnosis using noninvasive, collectable samples such as sweat and urine is promoted as an alternative to blood-based diagnosis for future personalized healthcare and health maintenance on an individual basis.(5) The American College of Sports and Medicine confirmed the difficulty in planning for specific hydration because a person's sweat rate and sweat electrolyte concentration vary with exercise tasks and weather conditions.(6) In managing dehydration, sweat must be easily and frequently monitored, and the quantity and quality of hydration must be determined on an individual basis.

Healthcare applications, such as monitoring hydration and heat stress, preventing dehydration, and managing self-health, have been the focus of numerous studies.(7–13) Previous studies have focused on sweat volume and its components, including electrolytes. The volume of sweat is primarily used as a guideline for hydration because it allows the direct observation of the degree of dehydration. Pavlov *et al.* provided a new algorithm for estimating sweat volume using machine learning models based on values from sensors in commercial smartwatches.(7) Drexelius *et al.* reported on an optical approach to monitor individual sweat glands using an infrared camera for sweat volume evaluation.(8)

Sodium and potassium, which are abundant components in sweat, play crucial roles in hydration monitoring through electrolyte balance and possess other important functions. Sodium loss through sweating is associated with heat cramps.(9) In addition, sodium and potassium maintain cell osmotic pressure. Potassium affects muscle contraction and nerve excitability. A patch electrochemical sensor and a hydrogel touchpad-based sweat biosensor can be used to measure sweat components such as electrolytes (Na^+, K^+, and Ca^{2+}) and cortisol.(10–13) Although many of these sensors are small in size and light, they require support from smartphones or other devices to function. The construction of a real-time monitoring system solely with the sensor has not yet been achieved.

Here, a multi-wavelength NIR spectroscopic method was investigated for the evaluation of sweat components in standalone devices, including small stationary devices and smartwatches. NIR spectroscopy can enable maintenance-free, nondestructive, and real-time monitoring. To achieve portable NIR devices, using a limited number of wavelengths with LEDs or photodiodes is necessary to monitor target components instead of a monochromator. To the authors' knowledge, there have been no previous reports of measuring electrolyte concentrations in biological fluids such as sweat using near-infrared spectroscopy, given that ions themselves do not absorb near-infrared light. In our previous work, we demonstrated a method for accurately evaluating urinary components such as urea, creatinine, and sodium using multiple wavelengths of near-infrared light. This approach exploits the fact that the presence of ions around water molecules alters water's intrinsic absorption. By actively leveraging the wavelength region where water absorption dominates solute absorption and exhibits a negative differential spectrum, we achieved high-precision evaluation of the sodium concentration.(14,15) In this study, we extend this method to sweat samples, aiming to predict the sodium concentration in sweat. In demonstrating the feasibility of quantifying electrolyte concentrations in sweat using multi-wavelength NIR spectroscopy, near-infrared spectral analysis was conducted on two types of electrolyte (Na^+ and K^+) in water. The wavelengths suitable for quantitative analysis were also investigated across a broad range of 1000–2300 nm using multiple regression analysis. However, this method is designed to be applicable to situations involving heavy sweating, such as during exercise or in hot environments.

2. Data, Materials, and Methods

2.1 Materials

Ultrapure water with 18.2 MΩ·cm was obtained by using the ultrapurification water system UL-Pure (Komatsu Electronics Co., Ltd, Japan), which was used to prepare the aqueous solution. Electrolyte concentrations in aqueous solution samples were adjusted with sodium chloride and dipotassium hydrogen phosphate (special grade, Hayashi Pure Chemical Ind., Ltd., Japan). The actual concentration of the prepared solution was determined using the LAQUAtwin pocket water quality meters Na-11 and K-11 (HORIBA, Ltd., Japan). Spectrum 3 (Perkin Elmer Inc., USA) was used to record the NIR spectra of the samples and ultrapure water. The spectrometer was equipped with a water-heating jacket with demountable liquid cells (Specac, Ltd., UK) for temperature control.

2.2 Sample preparation and spectral measurements

Several reports have been found on sodium and potassium concentrations in sweat,(16–18) and the values vary widely (Na^+, 54.0–276 mg/dL; K^+, 7.6–156.0 mg/dL) depending on the experimental conditions, such as the site of sample collection and exercise load. From these reference values, the sample concentrations used in this study ranged from 50 to 250 mg/dL for sodium, in 50 mg/dL increments, and from 30 to 150 mg/dL for potassium, in 30 mg/dL increments. Each sample concentration was measured at least three times using LAQUAtwin, and the most frequent value was used as the actual concentration. LAQUAtwin was calibrated every 10 measurements using two calibration solutions of different concentrations per cation.

Spectral measurements were performed as described in our previous reports.(14,15) All samples were triplicated, and spectra were measured in the wavelength range of 700–2501 nm with a resolution of 1.7507 nm using the spectrometer, alternating between ultrapure water and samples. The specific procedure was as follows. After circulating in constant-temperature water at 25 °C in the water-heating jacket and waiting for 30 min, a liquid cell with an optical path length of 0.5 mm was filled with ultrapure water or samples. Then, the transmittance spectrum was measured 16 times in succession. Afterward, the average of the 16 measurements was taken as the measured value. The approximate volume of the cell with a 0.5 mm path length was 0.135 mL. This did not account for any additional liquid in the filling port areas.

2.3 Analysis

The experimental data were analyzed using MATLAB (version 9.12.0.1927505, R2022a). All spectra were smoothed using a Savitsky–Golay filter. Differential absorbance (ΔAbs) was calculated by subtracting the ultrapure water spectrum from sample one and normalizing all spectra to the value at 1060 nm, where water does not absorb. ΔAbs at each wavelength and actual concentrations were used to evaluate concentrations by multiple regression analysis. On the basis of a previous report,(14,15) 1023 wavelength combinations were analyzed using 10 wavelengths (1400–2300 nm in approximately 100 nm increments). The wavelengths and their number were selected from the 1023 combinations based on the standard error of prediction (SEP) and the correlation coefficient (γ). SEP is the prediction error of the residual between the optical evaluation and the reference. Furthermore, the effects of changing the number of wavelengths and their combinations on the SEP and γ were examined.

3. Results

3.1 Spectra of NaCl and K_2HPO_4 solution

Figures 1 and 2 show typical spectra of NaCl and K_2HPO_4, respectively. As shown in Figs. 1 and 2, ΔAbs fluctuates considerably and becomes unstable at around 1900–2000 nm, where the absorbance of water is large. Figure 1 shows the absorption of ionized Na^+ in aqueous solution with changes in solute concentration. Spectral changes such as decreases near 1400, 1500, and 2000 nm, and increases at 1800 and 2200 nm were observed. The K_2HPO_4 spectra shown in Fig. 2 indicate the absorbance wavelength equivalent to the NaCl spectra; however, the peak wavelength is shifted to the left at 1400–1500 nm compared with the NaCl spectra. In the range of 1800 nm and 2100–2200 nm, the change in ΔAbs is larger than that in NaCl. In both figures, negative peaks indicate regions of greater absorbance by the O–H band of water than by the solute.

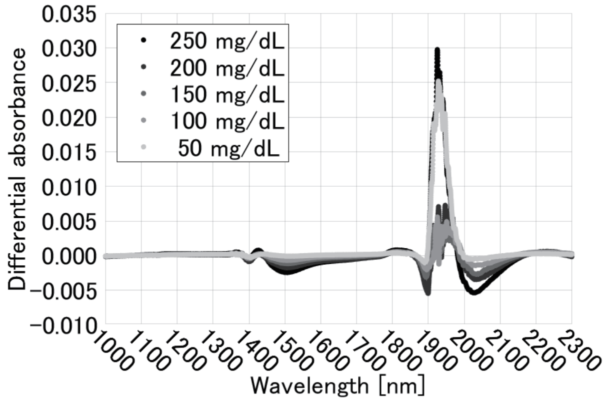


Fig. 1. Differential absorbance spectra of NaCl solution with five levels of solute concentration.

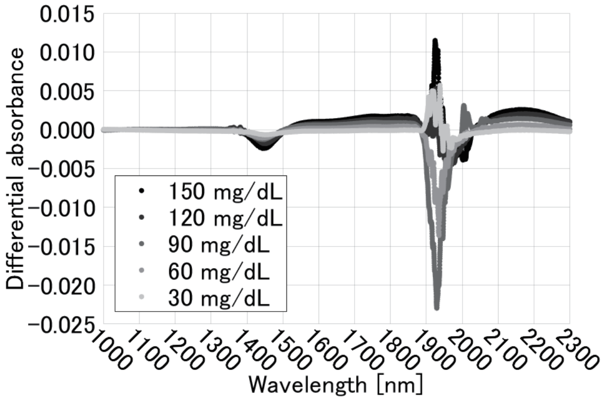


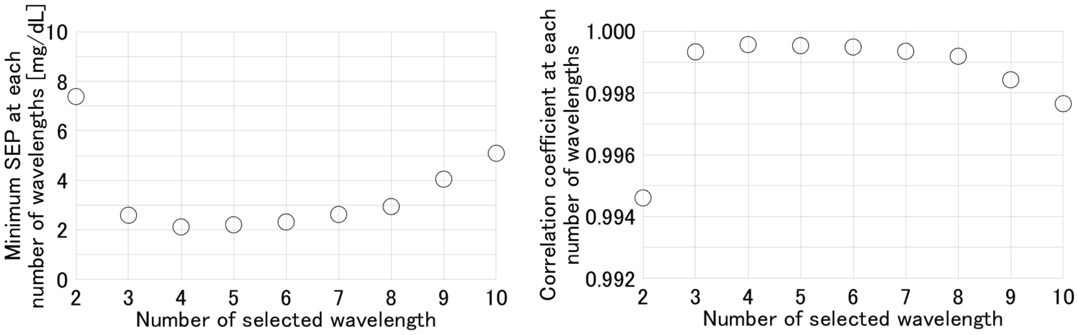
Fig. 2. Differential absorbance spectra of K_2HPO_4 solution with five levels of solute concentration.

3.2 Selection of wavelengths

In selecting the combinations of wavelengths with high accuracy for concentration evaluation, the correlation coefficient and SEP between the actual measured concentration and the evaluated concentration for each combination were demonstrated. Figures 3 and 4 show the minimum SEP and correlation coefficient at each number of wavelengths of Na^+ and K^+. In Fig. 3(a), the SEP value of 2.116 for the combination of the four wavelengths in the Na^+ evaluation is sufficiently small relative to the concentration range of 50–250 mg/dL. The correlation coefficients were elevated regardless of the number of wavelengths used; however, the highest value ($\gamma = 0.9996$) was obtained at four wavelengths, as shown in Fig. 3(b). This trend is consistent with the potassium evaluation shown in Fig. 4(b), and the smallest SEP was at five wavelengths, as shown in Fig. 4(a). The highest correlation coefficient ($\gamma = 0.9995$) was obtained using five wavelengths, where SEP was the smallest.

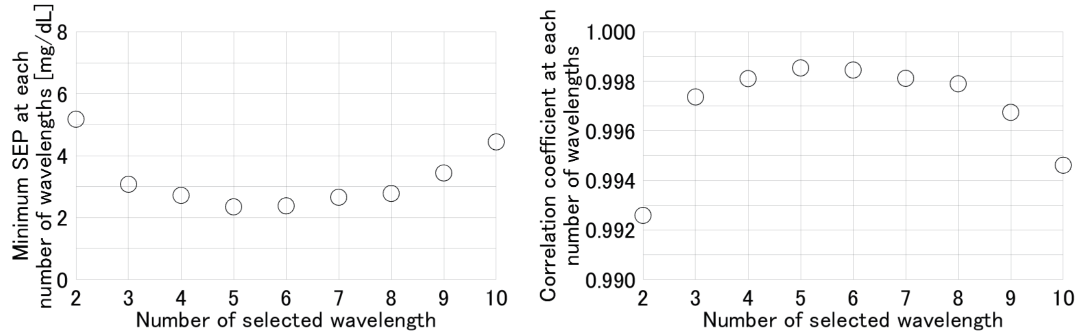
3.3 Evaluation of Na^+ and K^+ concentrations

Considering that the evaluation accuracy is high when using four wavelengths for Na^+ and five wavelengths for K^+, the concentration evaluation results were presented using these wavelengths (Fig. 5). Figures 5(a) and 5(b) show the correlation plots between the actual concentration and evaluated concentration using four wavelengths for (a) Na^+ and (b) K^+ both in single solutions. High evaluation accuracies were obtained because the correlation coefficients (γ) are >0.998, and SEPs are sufficiently low, being <2% of the set maximum concentration in both figures. Figure 6 shows the correlation plots using two wavelengths for Na^+ and K^+. Consequently, high evaluated accuracies of >0.993 for the correlation coefficient were obtained using only two wavelengths.



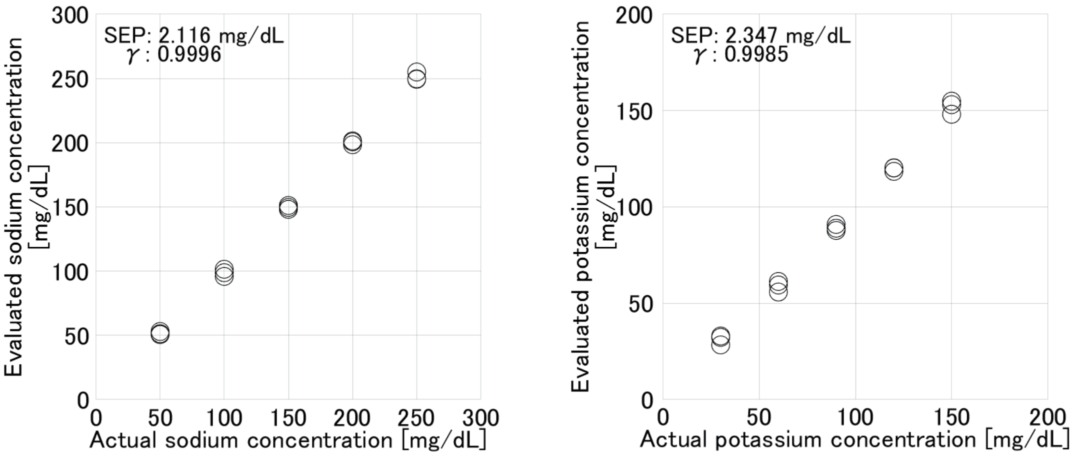
(a) (b)

Fig. 3. Minimum SEP and correlation coefficient for Na^+ at each number of wavelengths. (a) SEP values used for wavelength selection and (b) correlation coefficient. SEP is 41.04 and the correlation coefficient is 0.817 when using one wavelength (1500 nm).



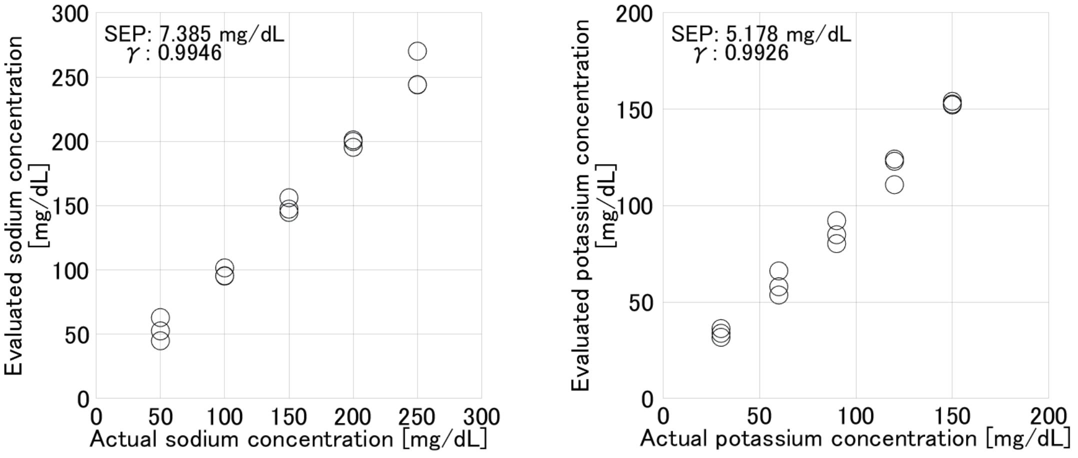
(a) (b)

Fig. 4. Minimum SEP and correlation coefficient for K^+ at each number of wavelengths. (a) SEP values used for wavelength selection and (b) correlation coefficient. SEP is 41.26 and the correlation coefficient is 0.380 when using one wavelength (2000 nm).



(a) (b)

Fig. 5. Correlation plot between actual and evaluated concentrations using four wavelengths for Na^+ and five wavelengths for K^+. (a) Results for sodium using 1400, 1700, 1800, and 2000 nm. (b) Results for potassium using 1400, 1500, 1600, 1800, and 2000 nm.



(a) (b)

Fig. 6. Correlation plot between actual and evaluated concentrations using two wavelengths. (a) Results for sodium using 1700 and 1800 nm. (b) Results for potassium using 1500 and 2100 nm.

4. Discussion

The wavelength combinations for electrolyte evaluation were selected by comparing each SEP value and correlation coefficient shown in Figs. 3 and 4. The number of wavelengths used was selected to be as small as possible considering the future goal, which is the construction of a compact device using an LED light source. The highest evaluation accuracies were obtained using four wavelengths for Na^+ (1400, 1700, 1800, and 2000 nm) and five wavelengths for K^+ (1400, 1500, 1600, 1800, and 2000 nm). These wavelengths exhibited remarkable absorption (Figs. 1 and 2), particularly at 1400 and 2000 nm for Na^+ and 1400, 1500, 1600 and 1800 nm for K^+.

Here, the assignment of differential absorption peaks at these wavelengths is considered. The observed peaks are attributed to the hydration states because Na^+ and K^+ do not show absorption in the NIR region.(19–22) In the NIR spectrum of water, an overtone peak of the O–H bond is observed at around 1400 nm (approximately 7000 cm^{-1}),(21) and broad absorption peaks are attributed to the combination bands of $\nu 2 + \nu 3 + \nu_{\mathrm{libration}}$ and $\nu 2 + \nu 3$ in the 1600–1800 nm (around 5600 cm^{-1}) and 1800–2200 nm ranges (4800–5400 cm^{-1}), respectively.(19,20,22) These peaks change with the concentration and type of electrolyte used for Na^+ and K^+ detections in this study. In particular, the O–H bond wavelength of 1400–1600 nm is shown to be useful for distinguishing Na^+ and K^+, and 1500 nm and 1600 nm were used for only K^+ as a result. In this study, high correlation coefficients ($\gamma > 0.993$) and low SEP values were confirmed for Na^+ and K^+, respectively (Figs. 5 and 6). These results indicate that the optical method of evaluating electrolyte concentration using a single wavelength is comparable to the measurement method using a commercial ion meter. In contrast, high evaluation accuracies were confirmed, although two wavelengths were used (1700 and 1800 nm for Na^+; 1500 and 2100 nm for K^+; Fig. 6). These evaluation accuracies demonstrated significantly higher correlation coefficients and lower SEP than the results obtained using a single wavelength. Considering the construction of a practical system, a reduction in the number of wavelengths may reduce the number of necessary light sources, such as LEDs, which may lead to a smaller size and lower cost of portable analytical devices. When the number of wavelengths used was reduced to two, we were still able to evaluate each electrolyte with high accuracy. Therefore, the results of this study may contribute to the construction of miniaturized systems.

We discuss the challenges that need to be addressed for the practical application of this system. First, the amount of sweat that can be collected is a concern. According to several reports on the sweat rate of athletes, total body sweat loss can range from 0.5 to 2.0 L/h (8.3–33.3 mL/min).(23,24) Assuming that sweat is collected only from the forearm, which accounts for approximately 9% of the total body surface area, the estimated sweat collection rate would be around 0.75–3.0 mL/min. Since the cell volume of our system is 0.135 mL, it may be difficult to apply it to conditions with extremely low sweat rates, such as during rest or sleep, although application during exercise is possible. There is room for improvement regarding the optical path length of the cell, and reducing the path length might enable us to decrease the required liquid volume. Second, in practical applications, the accuracy of concentration evaluation may be reduced due to contamination of the cell surface by sebum, skin flakes, and sweat crystallization. It is necessary to consider methods for filtering sweat itself and cleaning the cell. These two points will be clarified in future work.

5. Conclusions

In this study, the NIR spectroscopic evaluation of sodium and potassium levels was performed in water-based solutions. Our optical method used four or five wavelengths to evaluate two electrolytes in a water-based solution that simulates sweat with extremely high accuracy. Thus, the optical evaluation is strongly correlated to the reference, although Na^+ and K^+ do not absorb light. Our method also maintained high evaluation accuracy when the number of wavelengths used is reduced to two, making our method a practical technique for system construction. Therefore, the reduction in the number of wavelengths achieved in this study may enhance the practicality of miniaturizing sweat component measurement systems, potentially enabling convenient dehydration prevention and athlete performance management.

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