Measurement of Skin Surface pH with a Non-invasive Dry pH Sensor

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Abstract. Recent reports suggest that skin barrier function and atopic dermatitis are related to skin surface pH. We are developing a portable multifunctional skin measurement system for evaluating data such as skin pH and water content. The system uses a non-invasive method for measuring the skin’s surface pH and does not require addition of water. Previously, we reported a flat, dry pH sensor based on the Nernstian response that was fabricated by ion plating. When the sensor was used on the skin, the voltage was constantly elevated because of water evaporation from the skin. Herein, we measured the skin surface pH with the dry pH sensor and a glass electrode to compare non-invasive measurements and measurements with added water. The sensor was tested by using a standard pH solution and a correlation between pH and voltage was found. All experiments were carried out on the same region of the left forearm of healthy male subjects at constant room temperature and humidity (23 °C, 30% RH). Skin surface pH was measured for 2 min with the dry electrode and with a glass electrode, and then the skin water content was measured. The increase in voltage caused by water evaporation from the skin was subtracted from the dry pH sensor results. The skin surface pH was different between the non-invasive dry sensor and the conventional sensor. The response of the pH sensor voltage was affected by skin water evaporation and by water-soluble substances in the stratum corneum.

Keywords: Skin surface pH, flat dry-pH-Sensor, measurement, pH

1. Introduction

Human skin consists of three main types of tissues: the subcutaneous tissue, the dermis, and the epidermis, which includes the outer part of the skin called the stratum corneum (Fig. 1). Skin surface pH is measured on the stratum corneum, which contains various acids, such as amino acids, lactic acid, and fatty acids, as well as numerous other compounds that form the acid mantle. The acid mantle provides a defense mechanism against pathogenic microorganisms and plays an important role in skin barrier homeostasis [1], [2].

Measurements of the skin surface pH and water content of the stratum corneum are useful in many non-invasive techniques used to assess atopic dermatitis and the physical properties of the skin barrier objectively [3], [4]. In addition, common loss-of-function genetic variants of the epidermal barrier protein, filaggrin, are a major predisposing factor for atopic dermatitis [5], suggesting that lack of filaggrin is involved in the mechanism of atopic dermatitis. Recent research suggests that skin barrier function is related to the skin surface pH and this plays a role in atopic dermatitis [6], [7]. Therefore, the skin surface pH may reflect the skin’s barrier properties and it might be an important index for evaluating skin condition and health. We intend to develop a portable multifunctional skin measurement system for evaluating data such as skin surface pH, water content, and temperature. The system uses a non-invasive method for measuring the skin’s surface pH and does not require addition of water. Previously, we reported a dry pH sensor consisting of a...
platinum wire electrode and an Ag/AgCl wire electrode, based on the Nernstian response [8]. The voltage was constantly elevated during dry pH sensor measurements. We developed another flat, dry pH sensor based on the Nernstian response that was fabricated by ion plating. This paper describes the effect on the skin water content of measuring the skin surface pH with the dry pH sensor. The relationship between the pH and voltage was determined by using a standard pH buffer solution.

![Skin structure, skin surface pH and water evaporation](image)

**Fig. 1: Skin structure, skin surface pH and water evaporation**

### 2. Material and Methods

#### 2.1. Flat, Dry pH Sensor

A photograph of the sensor is shown in Fig. 2 (A). The electrodes are connected through copper tape, silver paste, and leads. A schematic cross-sectional view of the sensor film layers is shown in Fig. 2 (B). Base layers of titanium, platinum, and silver were prepared by ion plating. The titanium layer was used for improving adhesion of the platinum and titanium layers to the substrate. A silver chloride layer was prepared by anodic polarization. The reference electrode consisted of silver, silver chloride, and potassium chloride. The platinum surface functioned as the working electrode through the Nernstian response. p-Xylene, Nafion, and potassium chloride were prepared by chemical vacuum deposition. p-Xylene functioned as a selective membrane for protons. The poly(4-methyl-1-pentene) membranes were prepared by vacuum casting.

![Flat, dry pH sensor](image)

**Fig. 2: (A) Flat, dry pH sensor. Substrate dimensions: 25 mm² × 1.1 mm, electrode area: 5 × 10 mm. (B) Schematic cross-sectional view of sensor film layers. (i) Working electrode and (ii) reference electrode. TPX: poly(4-methyl-1-pentene); p-XY: p-xylene; Naf: Nafion**

#### 2.2. Measurements

The measurements were performed by using a DC microvolt ammeter (PM-18U, TOA Co. Ltd., Japan) with a personal computer equipped with an analog/digital interface and a C language measurement program. Zero offset calibration was carried out before measurements using two standard Ag/AgCl electrodes (RE-1B, BAS Inc., Japan) with 0.01 mol/L NaOH solution. The sensor was used to measure five pH buffer solutions (pH 1.68, 4.01, 6.86, 9.18, 10.02) on a sampling sheet (Y011, Horiba Ltd., Japan). Sampling time was about 0.1 s and the total measurement time was 120 s for the pH voltage response. The pH voltage response was treated as a moving average.

Figure 3 (A) shows the pH sensor voltage response as a function of time. The low and high pH solution responses exhibit some drift. However, the intermediate pH voltage responses were sufficiently stable. Fig. 3 (B) shows the relationship between the pH voltage responses over 30–60 s and the average response is
plotted as a linear approximation. We focused on the average values because the intermediate pH voltage responses were stable and the skin measurement took 120 s.

![Graph](image1.png)

Fig. 3: (A) Sensor voltage response as a function of time for various pH standard buffer solutions. (B) Relationship between pH and voltage responses (averaged over 30-60s)

All measurements were carried out on the same region of the left forearm of two normal male subjects (A and B) at constant temperature and humidity (23 °C, 30% RH). The subjects were asked to rest for about 15 min with the forearm exposed and with an earth connection on their wrist to reduce noise.

Non-invasive skin surface pH measurements with the dry pH sensor were performed for 2 min without added water and were repeated 5 times. The responses showed some instability; therefore, they were analyzed with a linear approximation for 3-8 s, 30-120 s and 90-120 s, with $R^2 > 0.9$ and standard deviation of < 2.5 mV. One response measurement was selected from each subject.

After addition of water, skin surface pH was measured with a skin pH meter (PH900, Courage + Khazaka Electronic GmbH, Germany). The glass probe had a flat surface membrane with a reference contact, and it was calibrated using buffer solutions with pH values of 4.01 and 6.86. For every measurement, the electrode was rinsed ethanol and ionized water. The average was taken of three measurements performed five times and the maximum and minimum results were removed.

Skin water content was measured by a Corneometer (CM825, Courage + Khazaka Electronic GmbH, Germany) in arbitrary units. Skin water evaporation was measured by keeping the probe in contact with the skin for 120 s to monitor water content. The probe is coated with a hydrophobic material, so that water evaporating from the skin is collected on the surface of the sensor.

### 3. Results and Discussion

The skin surface pH determined with added water was 4.6 for subject A and 4.7 for subject B. Fig. 4 shows the skin surface pH voltage response measured with the dry pH sensor. The response was elevated in both subjects. Our previous results suggest that the elevation was caused by the evaporation of the skin’s water [9]. Therefore, the elevated response was subtracted using the slope of the linear approximation for 90–120 s.

![Graph](image2.png)

Fig. 4: Non-invasive skin surface voltage response measurement with the dry pH sensor (subject A, B)
Figure 5 shows the skin surface pH measurements obtained with the dry pH sensor. The pH voltage response was obtained using following equation (where y is the voltage [mV] and x is the pH) according to the results in Fig. 3 (B).

\[ y = -33.3x + 273.1 \]

These results show that the dry pH sensor voltage response on the skin was not affected by water evaporation alone during the measurements. The skin pH at the surface of the skin results from water-soluble substances in the stratum corneum, including sweat, sebum, carbon dioxide [10], and natural moisturizing factor. Both subjects had almost the same pH values for the conventional skin pH meter, which required water addition. However, the skin surface pH measurements with the dry pH sensor were different from the conventional measurements. This suggests that the non-invasive method could affect other factors that determine skin pH.

4. Conclusion

A dry pH sensor for non-invasive skin pH measurements was investigated. The pH voltage response was good for standard pH solutions. We subtracted the effect of water evaporation during the non-invasive measurements using our sensor, and then converted the results to pH. The skin pH values obtained by the conventional probe that requires additional water and our dry probe were different. These results indicate that our non-invasive dry pH sensor may measure different skin condition parameters because the water-soluble substances in the stratum corneum affect pH. We are investigating the differences between our probe and the conventional probe by using other skin measurement parameters, such as water content and sebum.

5. References


