
16 Outside and Inside Skin pH

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16.1 INTRODUCTION

Nowadays, the importance of pH is considered with respect to many aspects of our lives. Its influence on the health and well-being is often mentioned in a sense of body’s internal environment, for example, the impact of pH of food on the digestive system. However, concerns about pH deal not only with the inside of the body, but also with its most external organ, the skin.

The pH-value of the skin surface has been investigated by many researchers since the end of nineteenth century. The acidic nature of the skin surface was first mentioned by Heuss in 1892.¹ In 1928, Schade and Marchionini² used the term “acid mantle of the skin” (säuremantel) for the first time. Since this, that phenomenon has become of great interest, and many studies trying to explain its function and the mechanism of formation have been carried out. Nevertheless, many questions remain unexplained.

Considerations about skin pH can be divided into two parts: the outside and inside skin pH. The former applies to the skin surface and the latter to the pH-profile across the epidermis. In the following chapter, the inside and outside skin pH is addressed, as well as its importance and influence on skin barrier function. A short review of methods used to measure the pH is presented as well.

16.2 APPLICABILITY OF THE TERM “SKIN pH”

According to the International Union of Pure and Applied Chemistry (IUPAC), pH is defined as the negative logarithm (base 10) of the activity of hydrogen ions (see [Equation \[16.1\]](#)), and it is

recommended to apply this definition to diluted aqueous solutions (≤ 0.1 mol/kg).³

$$\text{pH} = -\log_{10} a_{\text{H}}, \quad (16.1)$$

where a_{H} is the activity of hydrogen ions.

Considering the definition presented, the accuracy of pH measurements of the skin is questionable. There are two inconsistencies emerging from the definition of pH. First, the skin, especially the epidermis, is not a diluted aqueous solution. Moreover, various residues located on the skin surface may influence the readings, if conducted by devices not designed for existence of many different substances.

The second problem applies to the performance of readings itself. In many cases, when the pH of the skin surface is measured, a small amount of water is applied on the skin before the measurement. Hence, it is not the pH of the skin surface that is measured, but the pH of the aqueous solution on the skin surface.

Both issues are widely discussed by Rieger,⁴ who wrote that what is actually measured is “pH of the (extractable) water-soluble constituents of skin.” Due to that problem, Rieger proposed to call that measured value not “pH of the skin” but “pH on the skin” or “the apparent pH.” That issue is also raised and described by Parra and Paye in guidelines of European Group on Efficacy Measurement of Cosmetics and Other Topical Products (EEMCO).⁵

Despite mentioned considerations, it is widely accepted to use the terms “skin pH” or “pH of the skin” for describing the pH measured on the skin surface by various types of methods. Those expressions are also used in the rest of this chapter, in a meaning of pH-values obtained by any measurement technique. However, it is important to realize, that measured pH of the skin is not the pH in a precise analytical–chemical sense.

16.3 MEASUREMENT METHODS

Methods used to measure skin pH are, from the analytical point of view, of the same type as those for determining the pH values in aqueous solutions. The earliest studies about skin pH were conducted with colorimetric methods, using indicators that change color with pH. This method is complicated, involving collection of indicator solution from the skin. It was simplified by usage of indicator-impregnated strips (foil-colorimetry).^{2,5,6}

Potentiometric methods are easier to use and are nowadays the most frequently utilized to measure outside skin pH. They are also used to establish pH in deeper layers of the epidermis, by first exposing them, for example, by tape stripping.⁷ The most common potentiometric method is using the hydrogen ion-selective glass electrode with internal reference electrode, which is often called just “glass electrode.”^{6,8} The electrode is often planar-shaped to make it more easily applied on the skin.⁹

There are also new methods suggested recently, but they are not yet commonly employed.⁵ One of them involves ion-selective field effect transistor as a sensor, which requires smaller measurement area compared to the glass electrode.¹⁰ Other possible methods are electron spin resonance imaging and confocal microscopy.^{5,11,12} They require treatment of the skin with an indicator substance, which penetrates into the epidermis and allows the pH to be detected in several layers simultaneously.¹²

When measuring skin pH, several issues have to be remembered. First, the interpretation of results has to be done carefully, taking into consideration points described earlier concerning the applicability of the definition of pH on measurements on the skin. Second, one has to realize that there are many substances present on the skin surface like sebum and sweat, as well as material of exogenous origin, for example, cosmetic products, which all can influence the readings.

16.4 FORMATION OF THE pH-GRADIENT

Skin pH is regulated by many substances, shifting pH into lower values by their proton-donating properties. Outside pH is influenced by various substances secreted to the skin surface, like sweat, sebum, and Natural Moisturizing Factor (NMF). Those secretions of eccrine and sebaceous glands contain various acids, like lactic acid, butyric acid, pyrrolidone carboxylic acid (PCA), amino acids, and free fatty acids. Additionally, ingredients of exogenous origin such as metabolites of cutaneous microflora (e.g., free fatty acids) and cosmetic products, can be present.^{5,13–15} However, it seems that outside skin pH depends mainly on processes taking place in deeper layers of the epidermis.¹³

The formation of pH-gradient inside the epidermis involves several mechanisms and perhaps not all of them are discovered yet. Currently, it is believed that stratum corneum acidification is regulated by the cooperation of three endogenous mechanisms: histidine-to-urocanic acid pathway, phospholipids-to-free fatty acids pathway, and membrane antiporters.¹³ The two former mechanisms consist of formation of acidic substances: urocanic acid and free fatty acids, which have proton-donating properties. In histidine-to-urocanic acid pathway, urocanic acid is formed by the hydrolytic enzyme histidase from histidine, which is obtained from hydrolyzation of filaggrin. This pathway is believed to be the most important mechanism acidifying stratum corneum and also has importance for other metabolic processes in the skin.^{13,16} The next mechanism consists of formation of free fatty acids from phospholipids and is mediated by other hydrolytic enzymes — secretory phospholipases.^{13,15} The last mechanism involves membrane antiporters (NHE1), which extrude protons in exchange for sodium. It is responsible for acidifying the interface between stratum granulosum and stratum corneum and/or in lower stratum corneum.^{13,17}

16.5 OUTSIDE SKIN pH

Outside skin pH has been studied extensively since the first publication describing its acidic properties.¹ Methods used to determine the pH have changed with time, but results are comparable, showing that pH on the surface of healthy, undamaged skin of an adult is slightly acidic, about 5, varying from 4 to 6.^{5,14,18–20} It is important to realize that it is impossible to assign only one pH-value to the skin. Variations in outside skin pH appear to depend on many endogenous and exogenous factors such as anatomical site, sex, age, race, circadian rhythm, temperature, humidity, etc. However, studies published so far, often show contradictory results, and it is still not established which factors really have impact on pH and which do not. Few of those factors are described later. More detailed summaries can be found in reviews by Parra and Payne,⁵ Fluhr and Elias,¹³ and Rippke et al.¹⁴

Among anatomical sites, intertriginous areas (e.g., axillia) seem to have the highest pH of all body surfaces, having pH shifted toward neutral or even alkaline.^{6,13,21,22} Fluhr and Elias¹³ proposed that this is caused by decreased urocanic acid formation due to higher humidity of those regions or by sebaceous/eccrine gland distribution. The differences between other anatomical sites are not so clear. For example, measurements conducted by Fluhr et al.²³ on 14 volunteers did not reveal regional differences between abdomen, back, forehead, lower leg, and forearm. In another study, on 574 adults, pH on cheeks was found significantly higher than on forehead.¹⁸

The difference in skin pH between sexes is also questionable. Few studies show a difference, with men having lower pH than women,^{24–27} while others do not.^{18,28} It is suggested, that possible pH difference between men and women can be due to sex-hormones, which influence skin barrier function.¹³

Age is an important factor. Outside skin pH changes during the course of life. Infants have neutral or slightly alkaline pH of the skin surface just after birth. It starts to decrease from the first day of life, but it takes a month to obtain pH of about 5.^{13,29–34} pH remains almost constant during childhood and adult life and increases in elderly.^{13,18,35}

Few studies show that pH of some body areas is influenced also by circadian rhythm.^{36–38}

16.6 INSIDE SKIN pH

There is a pH-gradient through the epidermis, changing from acidic values on the skin surface to near-neutral pH of around 7.4 in viable epidermis.^{7,11,39} The profile of this gradient from the outside in, has been presented as increasing in a sigmoid way, preceded by an initial slight decrease of pH in the upper layers of stratum corneum.^{7,39} Recent research shows a more detailed picture. After the initial increase of pH, there is a dip to acidic values in the interface between stratum corneum and stratum granulosum, but inwards pH increases again, obtaining near-neutral values.^{13,40} This profile of the pH-gradient seems to be in accordance with the hypothesis mentioned earlier regarding the formation of low skin pH.

16.7 FUNCTION AND IMPORTANCE OF SKIN pH

Although the acidity of the skin was described long ago,^{1,2} its importance and function is still not fully understood. Studies conducted until now reveal the picture of a complex phenomenon, regulated by various mechanisms and fulfilling many different functions.

Since the very beginning, the acidic pH has been linked to skin microflora.^{2,41} The acidic pH is supposed to inhibit the growth of pathogenic microorganisms and keep the skin microflora in balance. If the skin pH is elevated, for example, after usage of alkaline soaps, prolonged occlusion, or in skin disorders like atopic dermatitis, the growth of pathogens increases.^{42–44}

Recent studies also reveal another important role of skin pH for the barrier function. The pH-gradient is essential for several enzymes located in the epidermis necessary for formation of the skin barrier. Deviation from optimal pH-values can influence their activity, and as a result, abnormal structure and function of stratum corneum may occur.^{13,45} One of the pH-dependent enzymes is proteases, responsible for degradation of desmosomes keeping corneocytes together.^{39,46–48} Another example is of the enzymes responsible for the formation of lipids necessary for skin barrier formation: ceramides, free fatty acids, and cholesterol.⁴⁹ β -glucocerebrosidases and acid-sphingomyelinases are enzymes transforming glucosylceramides into ceramides, and phospholipase A₂ is necessary to obtain free fatty acids.^{49–54} The activity of those enzymes is pH-dependent: β -glucocerebrosidases, cholesterol acyltransferase, and one of the acid-sphingomyelinases show higher activity at acidic pH.^{55–57} Neutral or alkaline pH is suitable for other sphingomyelinases and phospholipase A₂.^{55,58} The importance of pH for activity of mentioned enzymes and therefore for skin barrier, was shown in a recent study on mice. Perturbed skin barrier recovered normally when the skin was exposed to solutions buffered to an acidic pH, while initiation of the recovery was delayed when the damaged skin was exposed to neutral or alkaline pH. This delay in barrier recovery was suggested to be a consequence of a lower activity of β -glucocerebrosidases.⁴⁵

16.8 SKIN DISORDERS AND pH

In some skin disorders, a deviation from “normal” skin pH is observed. The skin of patients with atopic dermatitis has been shown to have elevated outside pH, especially on lesional areas, reaching values even above neutral.^{21,43} This can be explained by decreased level of proton-donating substances, for example, urocanic acid and amino acids.⁴³ Higher pH on the skin surface can facilitate growth of pathogenic micro-organisms such as *Staphylococcus aureus*, which causes problems in patients with atopic dermatitis.⁴³ Increased pH is also found in children with seborrheic dermatitis.⁵⁹

However, the change of pH occurs not only in the outside skin, but also in a gradient through epidermis as well. For example, in ichthyosis vulgaris, all of the pH-gradient is shifted toward higher values, when in x-linked recessive ichthyosis the effect is opposite.³⁹ This deviation in pH-gradient has big impact on enzymes located in the epidermis, whose activity is altered.

16.9 MOISTURIZERS, OTHER COSMETIC PRODUCTS, AND SKIN pH

16.9.1 pH OF COSMETIC PRODUCTS

The pH-values of cosmetic products are often stated on the packaging or mentioned in advertisements. Expressions like “pH neutral” or “skin friendly pH” are used, and their role is usually to convince customers about mildness and safety of the product, or its suitability for intended use, for example, low pH of a product for intimate hygiene or sensitive skin.

The majority of cosmetic products, such as creams and lotions — popularly called moisturizers — but also gels, liquid soaps, shampoos, etc., usually do not have extreme pH-values. The first reason for that is the aim to keep their pH similar to the skin pH, in order to avoid irritation. Another cause is to reduce the risk of separation of the product, because extremely acidic or alkaline environment can cause degradation of ingredients. Of course, there are cosmetic products available, with very high or low pH, which can cause irritation, but they are used for special purposes and are not supposed to be in contact with skin for a long time. The examples of such alkaline preparations are those for hair removal or making permanent waves. On the other end of the pH-scale, there are strongly acidic products used for deep skin peeling, for example, based on glycolic acid.

From the literature, little is known about the impact of cosmetic products on skin pH. Skin possesses buffering capacity, which protects it against changes of pH. It has been shown that after application of alkaline preparation, elevated outside skin pH decreases back toward acidic values.^{5,14,21} Such change of pH may occur also after application of a cosmetic product. This issue is barely mentioned in case of stay-on products, like moisturizers. Rinse-off cleansing products are investigated more often, in terms of their influence on skin pH and the correlation between their pH and the irritancy potential.

16.9.2 IMPACT OF STAY-ON PRODUCTS ON SKIN pH

Moisturizers and other similar stay-on products have often pH between 4 and 6. That pH-range is similar to skin surface pH and is often suitable for good physical stability of the cosmetic product. However, there are several moisturizing creams with world-wide acceptance, which have pH of about 7 or even 8, for example, those with stearic acid as the main emulsifier. Also skin protectants based upon zinc oxide often have an alkaline pH.

Stay-on cosmetic products contain ingredients that may affect skin surface pH. Various proton-donating substances are often incorporated into them, serving as pH-adjusters, humectants, or emulsifiers, etc. Sometimes they are the same as those occurring naturally on the skin surface, for example, lactic acid, PCA, amino acids, and free fatty acids. Alkaline substances, for example, sodium hydroxide and triethanolamine (TEA) are often used as well. After application of a cosmetic product on the skin, water and other volatile ingredients evaporate, while other substances stay on the surface and blend with those already present on the skin. As can be concluded from basic chemical knowledge, such application of acidic or alkaline substances may change skin surface pH, depending on the quantity of applied substances, their physicochemical properties, and the buffering capacity of the skin. The question is then, how big that impact is, in which direction pH is changed, and for how long that alteration persists. There is no straightforward answer for those questions, because each cosmetic product can influence skin pH in a different way. The problem of influence of stay-on products on skin pH is very complex and difficult to investigate due to several variables. It has not been studied thoroughly yet, but the growing awareness about skin pH prompts researches to investigate this issue in more detail.

The considerations mentioned earlier also bring up the subsequent questions that wait to be answered, for example, about the influence of moisturizers on pH-gradient inside the epidermis and the activity of enzymes, effect on skin barrier function and skin barrier recovery, or the difference in

impact in case of healthy or diseased skin. One of these issues was investigated in a study, where two moisturizers of two different pHs: one with pH 4.0 and the other with pH 7.5 were applied on skin exposed before to sodium lauryl sulphate (SLS). There was no difference in impact on skin barrier recovery between tested preparations, neither in the early nor in the late stages of the recovery, which suggests that the pH of the studied moisturizers did not have a major impact on the activity of the enzymes responsible for barrier recovery.⁶⁰

16.9.3 RINSE-OFF PRODUCTS AND THEIR pH

The effect of various types of rinse-off cleansing products on skin pH has been examined in many studies. There are many types of cleansing products available: liquid soaps, bar soaps, shampoos, cleansing foams, shower oils, etc. Although they differ in their appearance, consistency, foaming properties, or color, they all contain similar ingredients, the most important of them being surfactants, responsible for cleansing properties. There are many types of surfactants available. They exhibit a large variation in the irritancy potential and similarly do cosmetic products containing those surfactants.^{61–63}

The ability of cleansing products to change the skin pH in both adults and infants has been investigated. Several studies have shown that usage of alkaline soaps increases the outside skin pH.^{64–67} The impact of a long-term usage of an alkaline soap was studied by Korting et al.⁶⁴ Outside skin pH of volunteers using the soap repeatedly for few weeks was 0.3 units higher than of volunteers using acidic synthetic detergents. In the same study, short-term effect was studied as well, revealing that skin pH increased directly after washing the skin with both tested products and that increase was significantly higher in case of soap. That elevated skin pH decreased to initial values after about two hours.⁶⁴ Another study reported that pH increased 0.45 units when skin was washed with soap of pH 9.5 and slight increase was also found after usage of an acidic product of pH 5.5, as well as after washing the skin only with tap water (0.19 unit).⁶⁶ Such results suggest that use of any type of cleansing product may increase skin surface pH, even water. The mechanism behind the impact of cleansing products on outside skin pH is not explained yet. However, it seems that one reason may be that cleansing products remove various substances from the skin surface, among them those responsible for acidification, for example, NMF, lactic acid, free fatty acids, etc.

Similarly as in case of stay-on products, there are several questions waiting to be answered about the impact of pH of rinse-off cleansing products on the skin, its pH, and the skin barrier function. One of the issues investigated was the influence on skin microflora, showing that when skin pH increased after repeated use of an alkaline soap, the count of propionibacteria rose significantly.⁶⁴ Moreover, the irritancy properties of cleansing products have often been associated with their pH, but several studies show that there is no direct correlation between those two features.^{62,68–70} The reported difference in irritancy potential between cleansers with various pH may depend on the combination of surfactants and their inherent irritating capacity, rather than the pH of the products.⁶¹

The issue of pH of cosmetic products, their impact on the skin and the consequences of that impact are still not a well-known subject. Understanding of that problem can help not only in the invention of better cosmetic products but also in the avoidance of unnecessary or misleading marketing claims, which often confuse a customer.

16.10 SUMMARY

The knowledge about skin pH has been growing since the last few decades, but there is still much to be discovered. Many issues, for instance, the formation of pH-gradient or influence of various factors like sex or anatomical site on skin pH are still not fully explained. Better understanding of that phenomenon is of great importance for many types of research. In dermatology, it can help in treatment of various skin disorders, especially those connected to altered pH-gradient and impaired

skin barrier function. More information about skin pH is also necessary for research dealing with reconstructed epidermis and percutaneous drug penetration. Moreover, the knowledge about impact of various substances on skin pH would facilitate designing of better cosmetic and pharmaceutical products.

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