

*Review*

## **Potassium Wearable Potentiometric Biosensors and Related Sweat Collection Methods: A Review**

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**Abstract-** Wearable potentiometric ion sensors (WPISs) have emerged as exciting analytical platforms that combine chemical, material, and electronic advancements to provide physiological information during various human activities. The real possibility of wearing an analytical device with diverse configurations, such as sweatbands, patches, or garments, without disturbing the wearer's comfort has enabled potentiometric ion sensors to serve as both healthcare monitoring and improve the performance of athletes.

**Keywords-** Ion-selective electrodes (ISEs); Non-invasive monitoring; Potentiometric sensors; Wearable potentiometric ion sensors (WPISs); Potassium

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### **1. INTRODUCTION**

Sensors and biosensors give us crucial information about body hydration, electrolyte balance, and overall health status. Electrolytes are essential for various physiological functions, and monitoring their levels accurately is vital for diagnosing our body's conditions like dehydration, electrolyte imbalances, and metabolic disorders, they enable real-time monitoring of electrolyte levels, allowing for early detection of imbalances that can cause serious health

issues, also advances in sensor technology, including the integration of nanomaterials and wearable devices, have enhanced the sensitivity, selectivity, and multiplex capability of sensors for electrolyte detection [1-3].

Wearable electrochemical sensors for monitoring potassium levels in sweat and blood have become an important area of research in recent years they are emerging as powerful tools for continuous, real-time monitoring of various biomarkers in body fluids like sweat and blood. These sensors can monitor an individual's physiology and health status by detecting and tracking the levels of key analytes such as metabolites, electrolytes, and small molecules [4,5].

Sweat has become a popular target for wearable sensing because it is easy to collect and provides a wide range of information due to its correlation between the analytic concentration of sweat and blood. Sweat composition can be monitored continuously and non-invasively using wearable electrochemical sweat sensors. These sensors can detect biomarkers that can reveal a person's physiological status, athletic performance, or even the presence of diseases [6,7].

Wearable electrochemical sweat sensors allow for continuous, non-invasive monitoring of sweat composition, enabling the detection of biomarkers that can indicate physiological conditions, athletic performance, and even the presence of certain diseases [8-11].

Wearable electrochemical sensors for blood monitoring provide a minimally invasive way to monitor important analytes such as glucose, lactate, and other metabolites. Wearable electrochemical sensors can be connected to microfluidic and wireless communication modules for seamless data collection and health monitoring in real-time (Scheme 1) [12,13].



**Scheme 1.** Types of wearable potentiometric biosensors

Potassium is a vital electrolyte that is essential for muscle and nerve function as well as fluid balance in your body. High or low potassium levels can indicate several health conditions, such as kidney problems, adrenal gland issues, and some medications. Monitoring potassium levels via sweat and blood analysis can help in the early detection and treatment of these conditions.

## 2. WEARABLE POTENTIOMETRIC BIOSENSORS

Wearable electrochemical biosensors have become increasingly popular among athletes and patients, as they provide continuous monitoring of various biomarkers and physiological parameters. Two key factors that are important in the development of these sensors are portability and user-friendliness, they need to be compact, and lightweight so users can comfortably wear the sensors during their daily activities and in every place without any significant discomfort [14].

The development of wearable electrochemical biosensors has accelerated in recent decades, due to advancements in materials science, nano and microfabrication, and wireless technologies [15-17].

Early wearable biosensors were mostly focused on monitoring basic physiological parameters like heart rate and body temperature.

The integration of novel nanomaterials, such as carbon nanomaterials, metal nanoparticles, and conductive polymers, improved the performance and miniaturization of wearable electrochemical biosensors. These nanomaterials offer advantages like high surface area, enhanced conductivity, and improved catalytic activity, which increase the sensitivity, selectivity, and stability of the sensors [18,19].

Among electrochemical methods Potentiometric biosensors are the most popular, they are simple in design and require less power, are compact, and suitable for portable or wearable applications. Miniaturization could be done without significant loss of sensitivity. This enables the development of compact, wearable potentiometric biosensors.

The first potentiometric biosensor was developed in 1969 by Guilbault and Montalvo. They immobilized urease on an ammonia electrode to detect urea. Potentiometric biosensors, particularly ion-selective electrodes (ISEs), can achieve very low limits of detection for specific analytes when a highly stable and accurate reference electrode is used [20,21].

## 3. ALL-SOLID-STATE ION SELECTIVE ELECTRODES (AS-ISES)

The first ion-selective electrode was the creation of the pH electrode in 1906. The voltage changes in glass due to pH changes led to the development of the glass pH electrode, which is considered the first ion-selective electrode.

In the 1960s, new "specific ion electrodes" were being invented, these ISEs were developed for the detection of various ions, such as sodium, potassium, and chloride.

Ion-selective electrodes have become one of the most popular electroanalytical techniques, due to improving the selectivity, sensitivity, and stability with applications in various fields, including clinical, environmental, and industrial settings [22-26]. New materials and fabrication techniques can enhance their performance. The replacement of ion-to-electron transducing materials with inner-filling solutions can lead to improved sensor performance and application. The key limitations of conventional ion-selective electrodes (ISEs) that need to be overcome for portable analytical devices are sensitivity to evaporation of the inner filling solutions, which can affect the performance and stability of the ISE. The liquid inner filling solutions in conventional ISEs are vulnerable to changes in sample temperature and pressure, which can impact the ion-to-electron transduction and lead to potential drifts [27-29].

#### 4. INTEGRATION OF NANOMATERIALS IN ISE

The integration of nanomaterials in ion-selective electrodes (ISEs) has brought several benefits, particularly they can be used as ion-to-electron transducers and for the aim of increasing the surface area of the sensor.

Nanomaterials like carbon nanotubes, graphene, and conductive polymer nanocomposites have been widely used as solid-contact materials in all-solid-state ISEs, they transduce the ionic signal from the ion-selective membrane into an electronic signal so they improve the potential stability and reproducibility of the ISE [30].

The integration of nanomaterials in ISEs can significantly increase the surface area of the sensor and enhance sensitivity and detection limits.

Nanostructured materials, such as porous carbon, carbon microspheres, and nanocomposites, provide a large surface area-to-volume ratio, which allows for more efficient interaction between the analyte ions and the sensing interface so they can improve the sensor's response characteristics, such as detection limits and response times [31].

AS-ISEs do not require an internal filling solution, unlike conventional ISEs they can be fabricated using Conductive Polymers like Polypyrrole (PPy), it has been widely used as a solid contact material in ISEs, carbon Nanomaterials, Various types of carbon nanomaterials have been utilized as solid contacts in ISEs, including single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), graphene, fullerenes, and amorphous carbon, conducting nanomaterials, composite Materials, Chemically and Chemically and electrochemically reduced graphene oxide (CRGO and ERGO) have been investigated as solid contact materials in ISEs, these materials play a crucial role in enhancing the performance and functionality of solid-contact ISEs, contributing to advancements in stability, selectivity, miniaturization capabilities and time response and exhibit sufficient Nernstian slopes for the detection of alkali metal ions [32,33].

## **5. ANALYTE AND SOURCES**

### **5.1. Importance of potassium level in the human body**

Potassium is the main electrolyte found inside the body's cells, helping to maintain normal fluid levels and balance, it works in conjunction with sodium, to regulate fluid balance in the body. Potassium is essential for the proper functioning of muscles and nerves, as it helps regulate muscle contractions and nerve impulses and it has a crucial role in maintaining normal blood pressure. A diet high in potassium and low in sodium has been shown to help reduce the risk of high blood pressure, heart disease, and stroke [34].

### **5.2. Sweat as the source for detection of the body's electrolyte level**

Human sweat contains several key biomarkers and metabolites that are highly relevant to health and performance. Detecting these biomarkers from eccrine sweat glands offers numerous advantages over other bodily fluids.

Eccrine sweat glands are found in high density, with over 100 glands per square centimeter of the human body. Sweat is easily accessible and can be sampled efficiently without the risk of foreign contamination it allows for continuous, real-time monitoring of patients and athletes, providing valuable insights into their physiological status. Biomarkers and metabolites in sweat are less prone to degradation compared to other bodily fluids, ensuring the integrity of the measured data [35,36].

### **5.3. Correlation between blood and sweat potassium level**

There is a correlation between blood and sweat potassium levels, but the relationship can vary based on factors like exercise intensity and location of sweat collection. The research indicates that potassium concentrations in blood and sweat can be comparable, especially in the upper arm, during exercise. However, the potassium concentrations in sweat on the upper back may be lower compared to blood plasma. The decrease in blood potassium concentration following exercise is reflected in lower sweat potassium concentrations, suggesting a relationship between changes in blood plasma concentrations and sweat potassium concentration. Notably, the correlation between blood and sweat potassium levels may not always be significant, especially post-exercise, and can vary based on the specific conditions and locations of sweat collection. The potassium concentrations in sweat were generally within the range of 2-8 mM [37].

## **6. TYPES OF WEARABLE DESIGNS**

One of the primary challenges in wearable biosensors utilizing sweat is the collection of the proper amount of sweat from the skin surface while maintaining user comfort. This

challenge has led to the development of various types of wearables designed with different sweat collection methods and devices with comfortable attachments.

wearable potassium biosensors can be classified into different types based on sweat collection and their attachment methods on the skin:

### 6.1. Sweatbands

Sweatbands are commonly used platforms due to their ease of electrode implementation and sampling cell attachment. Typically, electrodes are fabricated on a flexible substrate and later affixed to standard bands, aligning with the disposable nature of the electrodes while maintaining the wearable aspect. Following this, the sensor is incorporated into the wearable design and is prepared for on-body testing. However, when utilizing sweatbands, individuals are limited to wearing the wearable ion sensor only on specific body areas where the bands can be securely fastened.

Sweatbands can collect sweat straight from the skin surface during exercise, or they can couple with Absorbent Materials, Liu et al. developed an ion-selective electrode (ISE) for the detection of potassium and pH monitoring in sweat. The device was designed in the shape of a headband, which incorporated a sweat channel. During exercise, sweat can effectively flow into the sweatband channel and reach the surface of the sensor, allowing the potassium-selective ISE (K-ISE) to measure the potassium concentration and pH of the sweat. The sensor had good stability and selectivity (1  $\mu$ M to 100 mM) for potassium ions [38].

Gao et al. introduced a wearable flexible integrated sensing array (FISA) through a flexible printed circuit board (FPCB) for simultaneous and selective screening of a panel of biomarkers in sweat. They used a thin rayon pad for collecting sweat on a flexible plastic substrate on a polyethylene terephthalate (PET) substrate, sensors were coupled with a polyvinyl butyral (PVB)-coated and carbon nanotubes reference electrode to maintain a stable potential in solutions with different ionic strengths. Poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) was used as an ion-to-electron transducer in the ISEs [39].

Criscuolo et al. introduced a headband-shaped multi-sensing platform with cotton fluidic for the detection of  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Pb}^{2+}$  on a Polyimide (PI) substrate, textile-based biosensing materials are low cost and they have high flexibility/wearability, it had good selectivity ( $10^{-5}$  to  $10^{-1}$ ) for potassium ion [40].

Marc Parrilla et al. developed a wearable biosensor for the detection of sodium and potassium ions in sweat on a Stretchable Substrate allowing it to be comfortably integrated into various wearable formats. The sensor incorporates multi-walled carbon nanotubes (MWCNTs) as a key component, it can enhance the sensor's performance and sensitivity. The stretchable biosensor can be attached to a wristband or integrated into a stretch fabric in direct contact with the skin also can be placed on an absorbent material to collect sweat directly from the skin surface [41].

## 6.2. Patches

The patch-type biosensors are designed to be worn directly on the skin, often on the upper arm or other accessible areas of the body. This direct skin contact allows for the continuous collection of physiological data. Patch-type biosensors can employ different methods for sample collection:

**Direct sample collection:** The patch can directly interface with the skin to collect biofluids like sweat or interstitial fluid.

**Absorbent materials:** The patch can incorporate absorbent materials like Whatman paper or cotton threads to wick and collect the sample.

**Microfluidic devices:** Some patch-type sensors integrate miniaturized microfluidic components to facilitate sample transport and analysis.

Choi et al. fabricated a wearable device for  $\text{Na}^+$ ,  $\text{K}^+$  and lactate monitoring in sweat. This device is made of an adhesive layer to attach it to the skin surface and microfluidic channel [42]. Kim et al. prepared low-cost 3D-printed flexible sensors with fluidic channels and PDMS substrate for the detection of  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Ca}^{2+}$  [35].

Yao Lu et. al fabricated a wearable self-powered-like sweat monitoring system with integrated micro-supercapacitors (MSCs) [43]. It was made of  $\text{NiCo}_2\text{O}_4$ /chitosan-based glucose sensors, ion selective membrane-based  $\text{Na}^+$  and  $\text{K}^+$  sensors, and  $\text{NiCo}_2\text{O}_4$ -based MSCs onto a flexible PET substrate as the power source of the sensor arrays. In another example, Baraiya et al. have demonstrated carbon-based electrodes on PET substrate for the detection of pH,  $\text{K}^+$ ,  $\text{Na}^+$ , glucose,  $\text{Cu}^{2+}$  and caffeine.

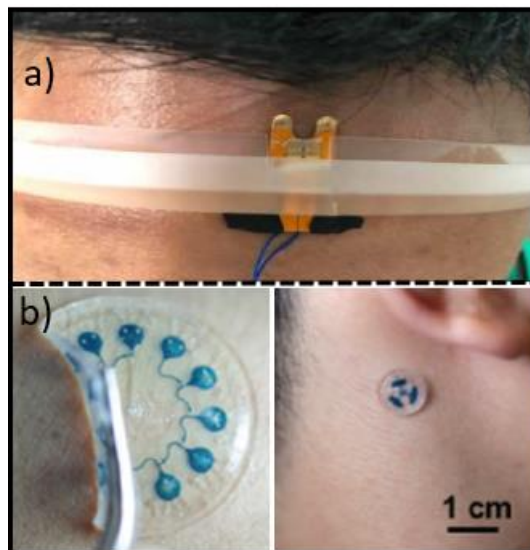
Alizadeh et al. made a device for detecting electrolytes during exertion, the patch incorporates a specialized fluidics system designed for effective sweat collection from the skin, even during moderate to high perspiration rates [44].

The fluidics system is made of laminated microfluidic channels formed from one or more hydrophobically-treated plastic films with patterned adhesives. This additive manufacturing technique, using a cutting plotter to pattern each layer followed by lamination, allows for rapid prototyping and easy implementation of changes to the channel geometry without the need for dedicated tooling. The device also includes a highly engineered electronics module for continuous monitoring of electrolytes in sweat during physical exertion. the patch can effectively wick and transport sweat from the skin surface to the sensing area, allowing for reliable and accurate real-time monitoring of electrolytes like sodium and potassium.

Cui et al. made a wearable sensor on PET substrate for pH and potassium analysis, they used Beta-CD functionalized graphene as the transducer, and Beta-CD prevents graphene from aggregation [45].

Liu et al. have developed a printed circuit board integrated ion-selective electrode (ISE) for monitoring potassium and sodium levels in sweat. This sensor is made of a gold (Au) electrode and PEDOT: PSS as the solid contact material. PEDOT: PSS is a conductive polymer that

exhibits redox capacitance, making it a highly effective ion-to-electron transducer in ion-selective electrodes. The use of a printed circuit board integration approach enables a compact and scalable design for the ISE (Figure 1) [46].



**Figure 1.** a) headband shape ISE [46]; b) patch-type ISE with an adhesive layer [42]

### 6.3. Textiles

Textile-based wearable biosensors have been developed for the detection of various analytes in sweat, including potassium. sensors incorporate sweat channels or microfluidic structures that allow sweat to effectively flow from the skin to the sensor surface.

Nicola Coppedè et al. introduced Textile organic electrochemical transistors (txOECTs), this was prepared by a series of consecutive functionalizations of the textile fiber, by applying the conductive polymer poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT: PSS) and the ion-selective membrane based on different ionophores to measure electrolytes in sweat. The textile OECT device was fabricated by soaking an acrylic textile thread with PEDOT: PSS. The ion-selective polymeric membrane was deposited on textile fibers [47] (Figure 2a).

### 6.4. Watch-shaped

Cao et al. made a smartwatch device for sweat  $K^+$  and  $Na^+$  monitoring, the device has a paper-based microfluidic patch with a three-dimensional structure. The patterns of this paper-based microfluidic patch were designed by CorelDRAW software and then printed by a wax printer, using Whatman #4 filter paper [48].

Pirovano et al. have made a watch-type (called SwEatch) wearable sensor for the detection of sodium and potassium ions in sweat during exercise. It is made of PEDOT-based Ion

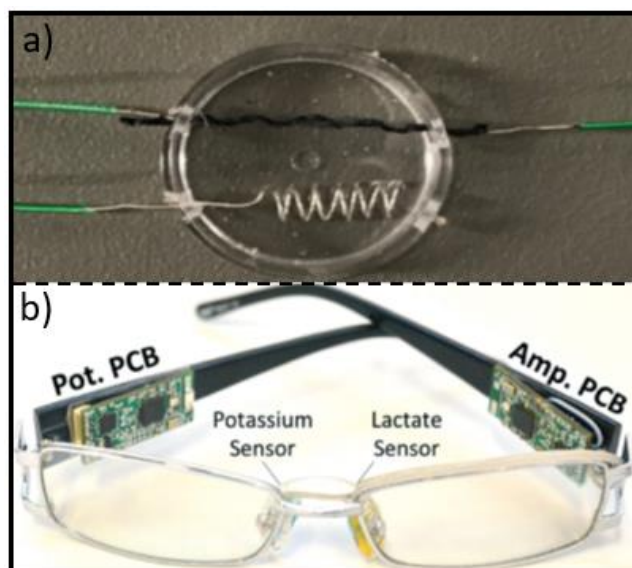


Selective Electrodes (ISE). This device has differentiating factors compared to previously developed SwEatch platforms owing to accommodating two-channel direct electrolytes monitoring and resistance to movement artifacts and the uptake and transport of the sweat, which was within the dual macro duct [49].

### 6.5. Other shapes

Sempionatto et al. designed a fully integrated eyeglasses wireless multiplexed chemical sensing platform for real-time monitoring of sweat potassium and lactate. Two printed circuit boards (PCBs) were placed on the different arms of the eyeglasses frame and sensors were screen printed on a PET substrate [50] (Figure 2b).

In another example, Golparvar et al. made a biosensor in the shape of a bracelet for the detection of potassium and sodium ions and the monitoring of body temperature [51].



**Figure 2.** a) textile-based ISE [47]; b) eyeglasses as an ISE [50]

## 4. CONCLUSION

In summary, this thorough review emphasizes the importance and progress of wearable sensors designed for detecting potassium levels in human sweat. These sensors exhibit promising capabilities in non-invasive and active sampling and continuous monitoring of potassium concentrations, thereby giving crucial information about personal health and physiological states. The types of wearable sensors and technologies explored in this review. As ongoing research in this domain advances, wearable potassium sensors are on the brink of transforming personalized health monitoring and playing a crucial role in the evolution of preventive and precision medicine.

## Declarations of interest

The authors declare no conflict of interest in this reported work.

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