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Textile-based sampling for potentiometric determination of ions

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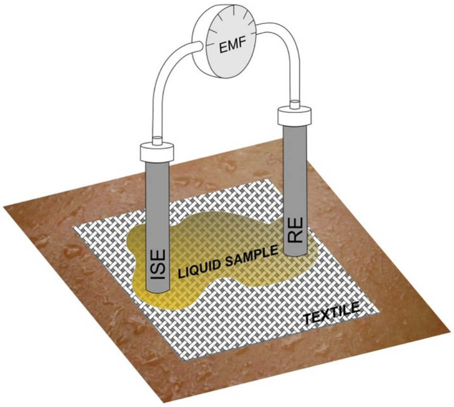
HIGHLIGHTS

- Development of textile-based sampling coupled with potentiometric ion sensors.
- Determination of analyte in micro-volume clinical samples.
- Determination of pH in environmental samples containing very little moisture.
- Low-cost method to screen textiles for utilities in on-body sensing applications.

GRAPHICAL ABSTRACT



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ABSTRACT

Potentiometric sensing utilizing textile-based micro-volume sampling was applied and evaluated for the determination of clinically (Na^+, K^+, Cl^-) and environmentally (Cd^{2+}, Pb^{2+} and pH) relevant analytes. In this technological design, calibration solutions and samples were absorbed into textiles while the potentiometric cells (ion-selective electrodes and reference electrode) were pressed against the textile. Once the liquid, by wicking action, reached the place where the potentiometric cell was pressed onto the textile, hence closing the electric circuit, the potentiometric response was obtained. Cotton, polyamide, polyester and their blends with elastane were applied for micro-volume sampling. The textiles were found to influence the determination of pH in environmental samples with pH close to neutral and Pb^{2+} at low analyte concentrations. On the other hand, textile-based micro-volume sampling was successfully applied in measurements of Na^+ using solid-contact sodium-selective electrodes utilizing all the investigated textiles for sampling. It was found that in order to extend the application of textile-based sampling toward environmental analysis of ions it will be necessary to tailor the physio-chemical properties of the textile materials. In general, textile-based sampling opens new possibilities for direct chemical analysis of small-volume samples and provide a simple and low-cost method to screen various textiles for their effects on samples to identify which textiles are the most suitable for on-body sensing.

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1. Introduction

Ion-selective electrodes (ISEs) are routinely used for the determination of ions in samples, such as blood serum and urine for Na^+, K^+, Cl^- concentrations and water for pH measurement. ISEs, however, are continuously investigated for their new utilities in other clinical, environmental, industrial and foodstuff samples [1]. For example, potentiometry has been trailed in the direct chloride determination in sweat and on the skin. In this particular study, the lack of proper sampling resulted in poor reproducibility of measurements, sweat evaporation, contamination of sample by the leakage from the liquid junction of the reference electrode, potential drift arising from the insufficient sensor contact with the skin and movements of the human subject [2]. Other studied applications of ISEs were within environmental analysis of heavy metals. This possibility has been discussed in several studies dealing with the lowering of the detection limit (LDL) [3–6]. However, the reliability of analytical procedures over time in such sample types make ISEs intensively investigated but not yet implemented in industrial scale [7,8]. Despite the application area, there is a clear need for tuning sampling and sample handling when ISEs are in use. Recently, simple and fast microfluidic sampling was developed by application of paper and its liquid absorbing properties to deliver small sample volumes (e.g., wet soil samples containing very little moisture compared to their solid content) to the detection place (ISEs pressed on the other side of the paper substrate) [9,10]. Moreover, in such protocols the development of solid-state reference electrodes and solid-contact ISEs opens the opportunity of applying potentiometric sensors in the environmental monitoring and wearable sensors [11].

Non-invasive wearable sensors are predominantly used for medical applications to measure analyte without intervention in the integrity of a body. They detect vital analytes in body fluids, such as tears, saliva and sweat using optical, piezoelectrical and electrochemical detection methods [12]. Owing to high performance, portability, relatively low cost and simplicity compared to other analytical techniques, electrochemical sensors dominate the wearable clinical diagnostics [13]. Up to date, textiles and paper substrates are the most commonly applied to integrate sensing elements with sampled surfaces, e.g., sensors on the skin [12]. Among many, worth mentioning are temporary tattoo papers for determination of sodium, ammonium and pH in sweat [14–16] or polyester, polyimide/lycra blend and GORE-TEX textile platforms for determination of chloride and sodium in sweat and nitroaromatic explosives for field-deployable security and soldier monitoring system [17–19].

The skin is an interface from which chemical or physical information may be obtained. As textiles are in constant contact with the skin, they are considered good platforms for wearable sensors [20]. Integration of the textiles with wearable sensors is realized in various ways. One is to integrate a sensor into the matrix of the textile, e.g., to knit a metallic element into the textile structure (textile electrode) [21]. Such sensors may be used then in integrated sensor platforms (e-textiles) with signal processing and handling for wireless health monitoring systems [22]. Another way is to deposit sensing elements on the textile substrates by the use of printing [20] and incorporating sensing elements in functional textiles, e.g., in a bandage for measurements of wound pH [23]. Finally, the sensing element may also be incorporated into other than textile platform, which in turn is in contact with the textile, e.g., microfluidic platform incorporated into textile for sweat pH monitoring [24]. Nevertheless, all textile integrated sensor platforms must perform well despite the mechanical stress induced on the textile over extended period of time [20].

In this work, textile substrates are used for micro-volume sampling of various analytes for the delivery of solution via wicking action to the detection place on the textile. Solid-state and solid-contact ion selective electrodes sensitive to Na^+, K^+, Cl^-, Cd^{2+}, Pb^{2+} and pH were used to evaluate the potentiometric sensor usefulness in applications in chemical analysis in clinical and environmental samples. In this design, ISEs are not permanently fixed to the textile substrates thus, if necessary, sensors may be used at different locations of textiles and can be used for continuous monitoring of ions or single checkup of ion activity at the sampling surface. The whole sensor platform is consisting of two separate parts, the textile-based sampling and sensors. This eliminates problems related to maintaining textiles in use, e.g., washing and allows using most advanced sensor technology as the sensors are used multiple times.

2. Experimental

2.1. Reagents and materials

$Cd(NO_3)_2$ (purity ≥ 99%) was purchased from Sigma–Aldrich (Steinheim, Germany), KCl (purity ≥ 99%), 4-*tert*-butylcalix[4]arene-tetraacetic acid tetraethyl ester (sodium ionophore X), valinomycin (potassium ionophore I), *tert*-butylcalix[4]arene-tetrakis(*N*,*N*-dimethylthioacetamide) (lead ionophore IV), tridodecylmethylammonium chloride (TDMACl), potassium tetrakis [3,5-bis(trifluoromethyl) phenyl]borate (KTFPB), sodium tetrakis (4-fluorophenyl) borate dihydrate (NaTFPB), 2-nitrophenyl octyl ether (*o*-NPOE), bis(2-ethylhexyl) sebacate (DOS), poly(vinyl chloride) of high molecular weight (PVC) and tetrahydrofuran (THF) were purchased from Fluka (Buchs, Switzerland) while $Pb(NO_3)_2$ (purity ≥ 99%) and potassium hydrogen carbonate ($KHCO_3$) (purity ≥ 99.5%) were purchased from Merck (Darmstadt, Germany). Artificial serum sample, abtrol was obtained from Thermo Fisher Scientific Oy (Vantaa, Finland). Aqueous solutions were prepared with freshly deionized water of 18.2 MΩ cm resistivity obtained with the ELGA PureLab ultra water system (High Wycombe, United Kingdom). Moreover, citrate buffer (pH 4), phosphate buffer (pH 7) and borate buffer (pH 10) were purchased from FF-Chemicals Oy Ab (Oulu, Finland). Textiles with six different fiber compositions were obtained from Uff clothing store, namely: 100% cotton manufactured by Puma SE (Herzogenaurach, Germany), 95% cotton and 5% elastane manufactured by Energetics (Bern, Switzerland), 100% polyamide manufactured by David (Helsinki, Finland), 90% polyamide and 10% elastane manufactured by Casall (Norrkoping, Sweden), 100% polyester manufactured by Willson (Chicago, USA) and 90% polyester and 10% elastane manufactured by H&M (Stockholm, Sweden). Before use, all textiles were vigorously washed with various liquids in a sequence: deionized water, 0.1 mol dm^{-3} HNO_3, deionized water, 99.5% ethanol and again with deionized water. Then textiles were left to dry at 70 °C for 3 h. Textiles were kept in closed polystyrene containers.

2.2. Electrodes

A flat-surface combination pH glass electrode (8135BN), Cd^{2+}-ISE (9448BN) and Cl^--ISE (9417BN) were obtained from Thermo Fischer Scientific (Waltham, USA) while a Pb^{2+}-ISE was obtained from Detektor s.c. (Raszyn, Poland). Ion-selective electrodes for Cd^{2+}, Cl^- and Pb^{2+} were of solid-state crystalline type. Also, solid-contact electrodes for Na^+, K^+, Pb^{2+} and Cl^- were prepared and used. In our solid-contact design of ISEs, glassy carbon electrodes in a teflon body were firstly cleaned by polishing using mesh paper with 0.3 μm Al_2O_3, washed with deionized water and 99.5% ethanol, left in an ultrasonic deionized water bath for 300 s and finally washed with water and 99.5% ethanol and dried with nitrogen. Then, electropolymerisation of