



# Paper-based microfluidic sampling for potentiometric determination of ions



Grzegorz Lisak, Jingwen Cui, Johan Bobacka\*

Åbo Akademi University, Process Chemistry Centre, c/o Laboratory of Analytical Chemistry, Biskopsgatan 8, FIN-20500 Åbo-Turku, Finland

## ARTICLE INFO

### Article history:

Available online 21 July 2014

### Keywords:

Potentiometric sensors  
Paper-based sampling  
Ion-selective electrodes  
pH determination  
Analysis of foodstuff

## ABSTRACT

In this work, paper-based microfluidic sampling was used together with potentiometric determination of ions ( $\text{Cd}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Pb}^{2+}$ ) and pH. Calibration solutions and samples were absorbed into paper substrates and potentiometric detection was performed by placing solid-state ion-selective electrodes (ISEs) and a reference electrode in direct contact with the paper substrate. The paper substrate was found to influence the determination of  $\text{Pb}^{2+}$  at low concentrations, indicating complexation of  $\text{Pb}^{2+}$  by chemically active groups present in paper. Paper-based microfluidic sampling was successfully applied in measurements of pH in various foodstuffs and environmental samples by employing a conventional pH glass electrode. However, some influence of the paper substrate on the measured pH was observed for samples with pH close to neutral. Despite some limitations, paper-based microfluidic sampling with potentiometric sensing opens new possibilities for direct chemical analysis of specific sample types. The method described in this work is particularly interesting for analysis of small sample volumes with a high content of solid impurities and for analysis of e.g. liquid or moisture from polluted surfaces and foodstuff.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

In modern chemical analysis of ions it is recommended to minimize any pre-treatment and manipulation of the sample. Operations, such as dilution, pre-concentration, standard additions and even a time delay may influence the speciation of ions in the sample [1–3]. Ion-selective electrodes (ISEs) offer the possibility to continuously measure ion concentration (activity) in untreated samples, if disturbances due to electrode fouling can be resolved or diminished [4]. Currently, potentiometric ion sensors are applied in clinical-, process- and environmental analysis. ISEs are implemented routinely in urine and blood analysis. However, reliable determination of ions in blood serum and urine is possible only when applying strict measurement protocols and regular washing of ISEs by using cleaning solutions. Due to electrode fouling, routine measurements in most clinical, industrial and foodstuff samples are not straightforward [4–6]. To diminish problems related to fouling of ISEs, specific sampling methods must be introduced to allow measurement of ions and at the same time to protect the electrodes from interfering matter, e.g. larger solid impurities (industrial and foodstuff samples) or blood cells (clinical samples). From this point of view, the combination of ISEs with paper-based microfluidic sampling can be a promising option [7].

Paper is a well-studied substrate for fabricating low-cost and flexible electronic devices [8,9]. In chemical sensor technology, paper has been used mainly in disposable sensors and microfluidic paper-based analytical devices ( $\mu$ PADs) [10–20]. However, so far very few publications are available on potentiometric detection combined with paper-based microfluidics [7,21].

In the present work different types of paper substrates are applied in microfluidic sampling of small volumes followed by potentiometric detection of ions and pH in the samples that are absorbed into paper. The ISEs and the reference electrode are simply pressed against the paper substrate to detect the concentration or activity of the analytes that are transported into the paper substrate. This eliminates liquid handling (in the traditional way) during calibration and measurements as the electrochemical sensors themselves are not immersed into the original sample. Paper-based microfluidic sampling is studied in this work for the potentiometric determination of ions ( $\text{Cd}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Pb}^{2+}$ ) and pH by using crystalline solid-state ISEs and pH glass electrodes, respectively.

## 2. Experimental

### 2.1. Reagents and electrodes

$\text{Cd}(\text{NO}_3)_2$  (purity  $\geq 99\%$ ) was purchased from Sigma–Aldrich (Steinheim, Germany), KCl (purity  $\geq 99\%$ ) was purchased from

\* Corresponding author. Tel.: +358 22153246.

E-mail address: [johan.bobacka@abo.fi](mailto:johan.bobacka@abo.fi) (J. Bobacka).

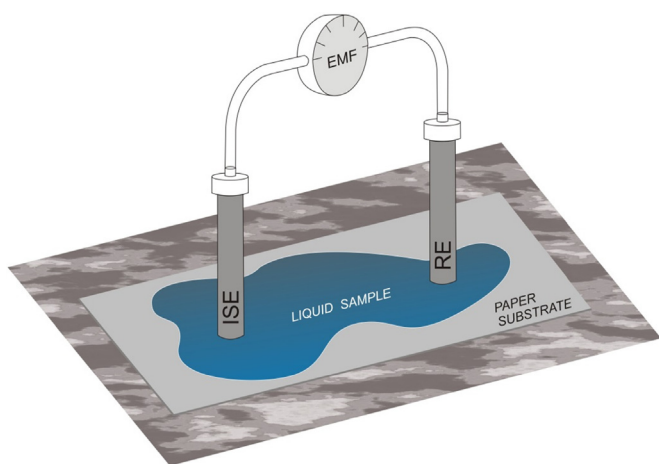


Fig. 1. Illustration of the paper-based sampling.

Fluka (Buchs, Switzerland) and  $\text{Pb}(\text{NO}_3)_2$  (purity  $\geq 99\%$ ) was purchased from Merck (Darmstadt, Germany). Citrate buffer (pH 4), phosphate buffer (pH 7) and borate buffer (pH 10) were purchased from FF-Chemicals Oy Ab (Oulu, Finland). Paper substrates used as sampling units were: black ribbon ashless filter paper which was obtained from Schleicher & Schuell GmbH (Dassel, Germany), hospital cotton tissue which was obtained from Metsä-Serla (Espoo, Finland), dirt-free tissue paper which was obtained from Katrin (Walon-on-Thames, UK) and delicate task wipes which were obtained from Kimberly-Clark (Irving, USA). A flat-surface combination pH glass electrode (8135BN),  $\text{Cd}^{2+}$ -ISE (9448BN) and  $\text{Cl}^-$ -ISE (9417BN) were obtained from Thermo Fischer Scientific (Waltham, USA), while a  $\text{Pb}^{2+}$ -ISE was obtained from Detektor s.c. (Raszyn, Poland). Ion-selective electrodes for  $\text{Cd}^{2+}$ ,  $\text{Cl}^-$  and  $\text{Pb}^{2+}$  were of solid-state crystalline type. A single junction reference electrode (6.0733.100) and standard combination pH glass electrodes (6.0238.000) were obtained from Metrohm (Herisau, Switzerland). Aqueous solutions were prepared with freshly deionized water of  $18.2 \text{ M}\Omega \text{ cm}$  resistivity obtained with the ELGA purelab ultra water system (High Wycombe, United Kingdom).

## 2.2. Potentiometric measurements with ISEs

Potentiometric measurements were performed using an EMF16 Interface (Lawson Labs Inc., USA). The Nernstian response of the  $\text{Cd}^{2+}$ ,  $\text{Cl}^-$  and  $\text{Pb}^{2+}$ -ISEs versus the  $\text{Ag}/\text{AgCl}/3 \text{ M KCl}$  reference electrode was verified by measurements in a conventional potentiometric cell, e.g. by immersing the electrodes directly into the bulk solution ( $10^{-1}$ – $10^{-6} \text{ mol dm}^{-3}$  of  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{KCl}$  and  $\text{Pb}(\text{NO}_3)_2$ , respectively). After a Nernstian response was observed ( $28.0 \pm 1.5 \text{ mV dec}^{-1}$  for divalent cations and  $-59.0 \pm 3.0 \text{ mV dec}^{-1}$  for  $\text{Cl}^-$ -ISEs), paper-based microfluidic sampling was investigated as shown schematically in Fig. 1. Four different paper substrates were studied, namely: black ribbon ashless filter papers (PS 1), dirt-free tissues paper (PS 2), hospital cotton tissues (PS 3) and delicate task wipes (PS 4). In this work, the paper substrates were positioned horizontally on the sample surface to minimize the transport distance of the liquid inside the paper (Fig. 1). This is in contrast to our previous communication, where the paper was positioned vertically so that only the lower end of the paper touched the sample [7]. Paper-based sampling was investigated here by placing  $200 \mu\text{l}$  of standard solutions onto a clean teflon plate (plain surface). The paper substrate ( $25 \times 25 \text{ mm}^2$ ) was placed horizontally on the drop to absorb the solution. Then, the solid-state ISEs and reference electrode were gently pressed onto the paper substrate to create a direct contact between the electrodes and the solution absorbed in the

paper matrix, followed by recording the EMF of the potentiometric cell. A new piece of paper was used for each standard and sample solution. Manual change of the paper substrate for each standard solution took about 30 s. The measurements were performed at room temperature. For comparison, ISEs were also calibrated in bulk solution (beaker-based measurements).

## 2.3. Determination of pH in various samples

Both standard (bulb-shaped) and flat-surface combination pH glass electrodes were used together with paper-based sampling for measurements of pH in three pH-buffer solutions (pH 4, 7 and 10). Prior to pH measurements the same pH buffers were used to calibrate the pH meter (Denver Instrument, Bohemia, USA). The paper-based sampling was done by all four types of paper substrates as described above for ISEs. However, the measurement protocol for standard and flat-surface combination pH electrodes was adjusted in order to obtain the most stable pH readings. For the standard combination pH electrode, where the active glass membrane is in a bulb shape, the paper substrate was first wet with  $200 \mu\text{l}$  sample solution and then transferred onto a polyethylene ring followed by gently pressing the bulb of the pH electrode inside the ring, creating sufficient coverage of the pH electrode bulb by the paper substrate. For the flat-surface combination electrode, the paper substrate was placed on the top of the  $200 \mu\text{l}$  sample solution drop followed by absorption of the drop into the paper matrix and pressing the flat surface of the electrode onto the paper substrate.

Foodstuff samples were purchased from the food market. Samples of drinks as well as juice from meat and plant products had a sufficient volume to allow a comparison between traditional measurements in the solution phase and measurements using paper-based sampling. Environmental samples were collected after a rainfall from the road, from a puddle in the ground, from a pile of snow mixed with soil, from moist soil, and from a mud pool. The samples were collected in polystyrene containers and the measurement of pH was done within 10 min from the sampling utilizing paper-based sampling with the flat-surface combination pH glass electrode. In this case, measurement without paper-based sampling was not possible due to the high content of solids (and thus low content of liquids) in the samples. Only an estimation of the pH without paper-based sampling was done for all samples (except the mud sample) by gently pressing the electrode to the surface of the sample. This, however, was not repeated multiple times since the solid impurities could damage the surface of the glass electrode.

## 3. Results and discussion

### 3.1. Paper-based sampling with $\text{Cd}^{2+}$ - and $\text{Cl}^-$ -ISEs

The potentiometric measurement set-up used in this work is shown in Fig. 1. The paper substrate was placed horizontally while electrodes were placed vertically to the sampling surface. In this way some potential sources of errors could be diminished, compared to the vertically positioned paper [7]. In particular, evaporation of standard and sample solutions from the paper substrates is minimized as the analyte only needs to be transported across the thickness of the paper substrates. This creates presumably a uniform distribution of analyte concentration along the whole paper substrate. Additionally, vertical positioning of the electrodes facilitates the use of commercially available liquid-junction reference electrodes that are characterized with a more stable potential and shorter response time than most of the currently available solid-state reference electrodes.

Fig. 2 presents the potentiometric response of a solid-state  $\text{Cd}^{2+}$ -ISE utilizing the paper substrate PS 1. The response of the

Download English Version:

<https://daneshyari.com/en/article/742511>

Download Persian Version:

<https://daneshyari.com/article/742511>

[Daneshyari.com](https://daneshyari.com)