Electrochimica Acta 140 (2014) 27–32

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Multicalibrational procedure for more reliable analyses of ions at low analyte concentrations

Grzegorz Lisak[a],*, Ari Ivaska[a], Andrzej Lewenstam[a,b], Johan Bobacka[a]

[a] *Laboratory of Analytical Chemistry and Centre for Process Analytical Chemistry and Sensor Technology 'ProSens', Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, 20500 Åbo, Finland*
[b] *AGH-University of Science and Technology, Faculty of Materials Science and Ceramics, Mickiewicza 30, 30-059 Cracow, Poland*

ARTICLE INFO

Article history:
Received 12 December 2013
Received in revised form 17 February 2014
Accepted 17 February 2014
Available online 3 March 2014

Keywords:
potentiometry
non-equilibrium sensors
ion-selective electrodes

ABSTRACT

Pb^{2+}-ISEs were used to demonstrate a new multicalibrational approach which gives comprehensive information about the response of a potentiomeric sensor. The method was used to study and optimize the non-equilibrium response of sensors, such as obtained with solid-contact ISEs used in time dependent conditioning procedure with recovery of the low detection limit at lowest analyte concentrations. The developed method allows better handling of non-equilibrium conditions in quantitative determinations of analytes. The multicalibrational approach with time optimization showed to be superior when compared to fixed measurement time approach using Pb^{2+}-ISEs at non-equilibrium in the determination of lead(II) in environmental sample.

1. Introduction

Owing to several advantages such as portability, low energy consumption, and small size ion-selective electrodes (ISEs) have actual potential in improving current analytical techniques in environmental analysis of ionic pollutants [1]. On the other hand, the pitfall associated with the need of recalibration, bio-fouling, and the reliability of analytical procedures over time make ISEs intensively investigated however not yet implemented in industrial scale [2,3].

The potentiometric response of every ISE is predominantly related to the potential formation at the ion selective membrane (ISM) | sample solution interface. This potential formation consists of two stages. First stage is the time dependent equilibration of the potential during which the electrode is under non-equilibrium conditions (often described as the response time of ISEs). Second stage is the time independent Nernstian response after the equilibration of the potential is established [4]. In more complex matrices (e.g. environmental and clinical samples) the potential formation may be disturbed and delayed by various unfavourable processes. Leaching, desorption, ion-exchange of the primary ion, and oxidation of the membrane surface ultimately result in uncontrolled release of the analyte to the sample from a conditioned membrane [5,6]. Additionally physical (e.g. adsorption), chemical (e.g. acidity/alkalinity, presence of interfering ions), and biological (e.g. bio-film formation) interactions with ion-selective membrane affect the response of ISEs. This is especially valid in measurements performed at low analyte concentrations in environmental samples [7–10]. Most of these interactions are highly time dependent, delaying equilibration of a potentiometric cell. In fact, in extreme situations equilibration of the potential may last for hours or may even be never attained [7,11–14]. Alternatively several of these hindrances can be overcame or diminished if the measurement is performed in a strict time domain. Thus, a mathematical model was introduced to visualize and predict the behaviour of ISEs under various conditions, considering low detection limit as well [15–17].

The possibility of using ISEs in environmental analysis has been discussed in several studies dealing with the lowering of the detection limit (LDL) [1,18–20]. In fact number of solid-contact ISEs were intensively studied to lower detection limit for environmental monitoring [21–26]. Recently, time dependent conditioning procedure to lower the detection limit of a solid-contact ISE was used to measure low concentrations of Pb^{2+} in synthetic samples. This method is based on non-equilibrium conditions as the constant influx of Pb^{2+} from the sample solution to a not fully conditioned ISM in the common methods determines the detection limit of the electrode [27,28]. This calls for a new approach how to deal with non-equilibrium sensors in measurements performed in environmental samples at low analyte concentrations.

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* Corresponding author.
E-mail address: grzegorz.lisak@gmail.com (G. Lisak).

http://dx.doi.org/10.1016/j.electacta.2014.02.091

In this work, solid-contact Pb^{2+}-ISEs based on polybenzopyrene doped with eriochrome black T as the contact layer were used to present the new approach for the dynamic description of the response of an ISE at non-equilibrium conditions. This multicalibrational procedure was developed to measure the ion concentrations in environmental samples more reliably. The concept of the procedure was used in the determination of lead(II) concentrations in environmental samples.

2. Experimental

2.1. Reagents

Lead (II) nitrate ($Pb(NO_3)_2$), sodium tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate (NaTFPB), poly(vinyl chloride) (PVC) high molecular weight, tetrahydrofuran (THF) were obtained from Fluka (Buchs, Switzerland). Potassium nitrate (KNO_3), potassium chloride (KCl), ethylenedinitrilo tetraacetic acid disodium dihydrate (Na_2EDTA), and eriochrome black T (EbT) were obtained from Merck (Darmstadt, Germany). Benzo(a)pyrene, 2-nitrophenyl octyl ether (o-NPOE), and acetonitrile (ACN) were obtained from Sigma-Aldrich (Steinheim, Germany). Nitric acid (HNO_3), 65% was purchased from Baker (Deventer, the Netherlands). All chemicals were of analytical grade. Aqueous solutions were prepared with freshly deionized water of 18.2 MΩ cm conductivity obtained with the ELGA purelab ultra water system (High Wycombe, United Kingdom).

2.2. Preparation of solid-contact ISEs

The polybenzopyrene films were polymerized on glassy carbon by cycling potential in an acetonitrile solution in the presence of eriochrome black T. The detailed procedure is described elsewhere [27]. The PVC-based membranes contained: 0.4% (3.80 mmol kg^{-1}) lead ionphore IV, 0.15% (1.69 mmol kg^{-1}) NaTFPB, 62.3% o-NPOE, and 37.15% PVC (weight %). A total weight of 200 mg of the membrane components were dissolved in 2 ml of THF. When the surface of the polybenzopyrene based electrodes was visually dry (2 hours after polymerization) the membrane cocktail was applied by drop casting. Portions of 10 μl of the membrane cocktail were applied every 10 minutes (longer if necessary, until visual evaporation of the solvent was observed) until final volume of 60 μl of the cocktail for a single electrode was attained. Electrodes were then left in open air for overnight evaporation of the residual solvent. Three electrodes were prepared according to the same procedure. The schematic picture of the electrode used in this study is shown in Fig. 1, left insert.

2.3. EMF measurements

The solid-contact lead selective electrodes was coupled with a double-junction electrode (Orion, Thermo Scientific- Environmental Instruments, Beverly, MA, USA) with outer 10^{-3} mol dm^{-3} KNO_3 and inner 1 mol dm^{-3} KCl solutions. All measurements were carried out in 100 ml disposable polystyrene beakers. Each beaker was soaked in 10^{-1} mol dm^{-3} HNO_3 for two days and washed with deionized water prior to use. Solid-contact electrodes were kept in a closed container in contact with air (at the bottom of the container was 20 ml of deionized water). Evaporation of water moistened membranes preventing them from over drying and cracking. When lose in detection limit of solid-contact electrodes occurred, a 24 h conditioning in 10^{-3} mol dm^{-3} Na_2EDTA was performed. The outer chamber of the reference electrode was washed first with 10^{-1} mol dm^{-3} HNO_3 deionized water and then with 10^{-3} mol dm^{-3} KNO_3. Between the measurements, the reference electrode was kept in 10^{-3} mol dm^{-3} KNO_3.

2.4. Determination of lead in environmental samples

A sample of groundwater was collected in the Finnish Archipelago from a puddle located 40 m north-west from the main shaft of an old silver mine. The details of sampling and sample handling are described elsewhere [9]. Zero-current potentiometry (direct determination) using the fixed measurement time and multicalibrational approach with time optimization were used to determine concentrations of Pb^{2+} in the environmental sample. For both potentiometric methods the calibration solutions were diluted using two Metrohm Dosino 700 instruments equipped with burets of 50 ml capacity (Metrohm, Herisau, Switzerland). The pumps were programmed to dilute tenfold the sample solution with freshly deionized water (18.2 MΩ cm) every 5 minutes. The obtained data were recorded with an EMF 16 Interface (Lawson Labs Inc., Malvern, PA, USA). Before measurements the electrodes were in contact with 10^{-3} mol dm^{-3} Na_2EDTA solution for 24 hours. Then the residual EDTA salt on the surface of ISM was removed by vigorously rinsing and keeping electrodes in deionized water for an hour. All the electrodes were preconditioned in 50 ml of 10^{-5} mol dm^{-3} $Pb(NO_3)_2$ for 20 minutes. Potentiometric measurement was run stepwise by tenfold dilution of the lead(II) solution, from 10^{-5} to 10^{-9} mol dm^{-3} $Pb(NO_3)_{2.}$ Each calibration solution contained a constant background electrolyte of 10^{-3} mol dm^{-3} KNO_3. For each concentration the electrodes were in the solution for 300 s under continuous stirring. After the potential reading was taken the calibration solution was diluted ten times. The calibration procedure was repeated until Nernstian response down to 10^{-8} mol dm^{-3} was obtained. Then the electrodes were rinsed with deionized water, moved to 50 ml of the environmental sample and *EMF* data was recorded for 300 s under continuous stirring. All the experiments were performed at room temperature (22-23 °C). The activity coefficients were calculated according to the Debye-Hückel approximation. All the *EMF* data were checked and corrected for liquid-junction potentials according to the Henderson equation. The same sets of *EMF* data were used to compare the determination of Pb^{2+} by two investigated potentiometric approaches. For fixed measurement time approach the *EMF* data was sampled after 300 s and was directly compared to previously obtained calibration curve. The uncertainty of the measurement was calculated from the three measurements. For the multicalibrational approach with time optimization first the potential formation in environmental sample and two limiting lead(II) calibration solutions (10^{-7} and 10^{-8} mol dm^{-3} Pb^{2+}) were investigated throughout 300 s of the measurement time (the Pb^{2+}-ISEs slope evolution in time). The time at which the electrode response was closest to the Nernstian response was used to draw the calibration curve and compare it to the *EMF* of Pb^{2+}-ISEs at the same time when measuring in environmental sample. The uncertainty was calculated from the electrode out of three measurements. For both methods, measurement time is here defined as the time that has elapsed after the electrode was exposed to the sample (calibration solution). All slopes of ISEs were reported as millivolts per tenfold change of lead(II) activity.

2.5. Inductively coupled plasma mass spectrometry (ICP-MS)

A Perkin Elmer-Sciex Elan 6100 DRC Plus Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to measure the total concentration of lead in deionized water after being in contact with atmospheric air, polystyrene breaker, the indicator and the reference electrodes. The analysis was performed at room temperature (22-23 °C).