ION SELECTIVE ELECTRODES FOR DETERMINATION OF LOW AND ULTRA LOW CONCENTRATIONS OF LEAD(II) IN NATURAL WATERS

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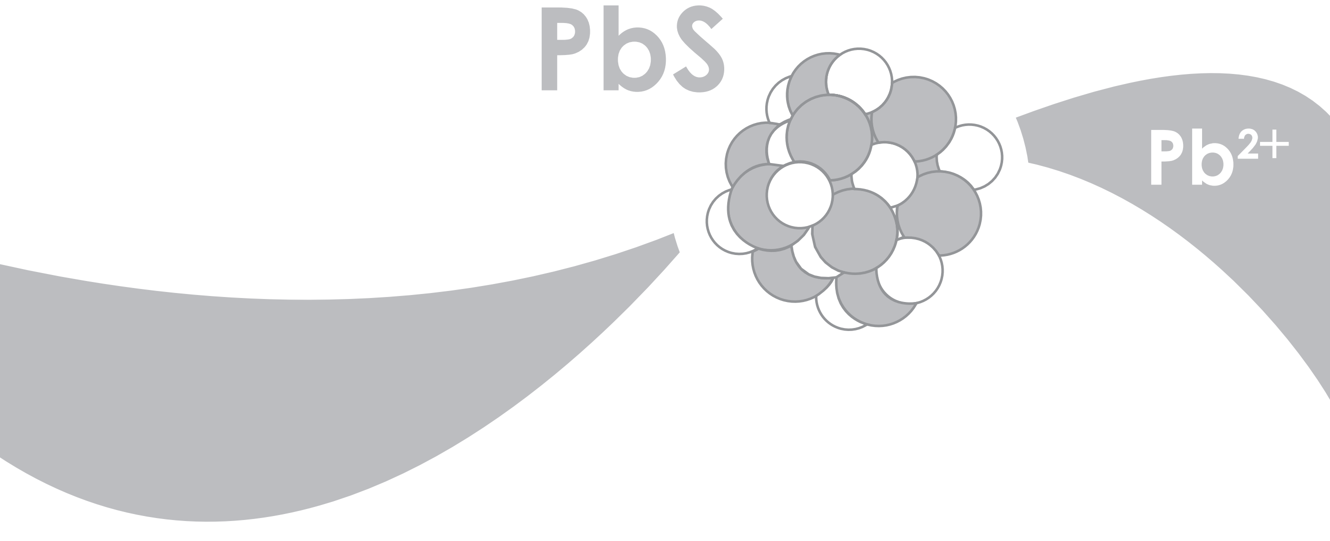

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Academic Dissertation

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To My Loving Family

Preface

The research work presented in this thesis was mainly carried out at the Laboratory of Analytical Chemistry at Åbo Akademi University as a part of activities of the Åbo Akademi Process Chemistry Centre. Funding from the Graduate School of Chemical Sensors and Microanalytical Systems (CHEMSEM), Stiftelsens för Åbo Akademi Forskningsinstitut, and the Rector of Åbo Akademi is gratefully acknowledged. Furthermore, I would like to acknowledge Magnus Ehrnrooth Foundation and Oskar Öflunds Stiftelse for financial support in conference participation and research visits.

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Åbo, April 2012

Abstract

Monitoring natural waters for toxic components is essential for human well-being. Since the content of pollutants occurring in natural ecosystems should be kept as low as possible, there is an ongoing search for analytical methods with ever lower detection limits. Nowadays, such analysis is realized by costly and sophisticated instrumentation which requires high maintenance. Owing to several advantages such as portability, low energy consumption, and relatively low cost, ion-selective electrodes (ISEs) may be considered useful in measurements of ionic pollutants. Such measurements are mainly possible when extending the sensitivity range of the ISEs by lowering the detection limit.

In this work, in order to lower the detection limit of Pb^{2+}-ISEs, polyacrylate co-polymer, PVC-based, and solid-state PbS/Ag_2S ion selective membranes were used. Although the polyacrylate matrix was introduced to diminish transmembrane ion fluxes in conventional types of Pb^{2+}-ISEs, no significant improvement in the detection limit was observed. Subsequently, a new conducting polymer material (polybenzopyrene doped with eriochrome black T) was applied as a sensing membrane/film. As a result it became possible to measure lead(II) easily down to 10^{-6} mol dm^{-3} Pb^{2+}. A significant improvement in the detection limit was achieved by applying this electroactive film as an ion-to-electron transducer in solid-contact Pb^{2+}-ISEs. In this way the lowering of the detection limit was achieved by concentration-time dependent conditioning and by the recovery of ISEs response at the nanomolar concentration range. The method was applied in the determination of Pb^{2+} in synthetic samples and was validated by the inductively coupled plasma mass spectrometry (ICP-MS) measurement.

Another approach to lower the detection limit of Pb^{2+}-ISEs was investigated with solid-state PbS/Ag_2S membrane electrodes. After lowering the parasitic processes at the solid-state membrane two methods were applied to improve the low detection limit (*LDL*): the controlled adsorption of the analyte on the electrode surface after pre-treatment of the electrode (*LDL*~ 10^{-8} mol dm^{-3} Pb^{2+}) and the tuned galvanostatic polarization of PbS/Ag_2S membrane (*LDL*~ 10^{-9} mol dm^{-3} Pb^{2+}). Due to the time limitations for a single measurement in the first method, the tuned galvanostatic polarization method was applied in measurements of Pb^{2+} in synthetic and environmental samples. PbS/Ag_2S membrane electrodes were successfully applied and validated by other analytical techniques (ICP-MS and differential pulse anodic stripping voltammetry; DPASV) in the quantitative determination of the lead(II) pollution in the environmental sample. In this thesis, novel approaches to lowering of the detection limit for measurements of low and ultra low analyte concentrations are presented.

Referat

Att övervaka förekomsten av giftiga komponenter i naturliga vattendrag är nödvändigt för människans välmående. Eftersom halten av föroreningar i naturens ekosystem bör hållas möjligast låg, pågår en ständig jakt efter analytiska metoder med allt lägre detektionsgränser. I dagens läge görs miljöanalyser med dyr och sofistikerad instrumentering som kräver mycket underhåll. Jonselektiva elektroder kan anses vara fördelaktigare vid mätningar av joniska föroreningar eftersom de har flera goda egenskaper som t.ex. bärbarhet och låg energiförbrukning, och dessutom är de relativt kostnadseffektiva. Att använda jonselektiva elektroder vid miljöanalyser är möjligt om deras känslighetsområde kan utvidgas genom att sänka deras detektionsgränser.

För att sänka detektionsgränsen för Pb^{2+}-selektiva elektroder undersöktes tre olika typer av jonselektiva membraner: en polyakrylat-kopolymermembran, en PVC-baserad jonselektiv membran med ett elektriskt ledande polymermaterial som fast kontakt och en fast-fas PbS/Ag_2S jonselektiv membran. Trots att målet med att införa en polyakrylatmatris i konventionella Pb^{2+}-selektiva elektroder var att minska på jonflödet inne i den jonselektiva membranen, och därmed sänka detektionsgränsen, kunde ingen tydlig förbättring av detektionsgränsen observeras. Därnäst undersöktes ett elektriskt ledande polymermaterial (polybenzopyren dopad med eriokrom svart T) som jonselektiv membran. Med denna membran var det möjligt att mäta bly(II)-halter ända ner till 10^{-6} mol dm^{-3} Pb^{2+}. En ytterligare förbättring av detektionsgränsen kunde uppnås då Pb^{2+}-selektiva elektroder konstruerades med denna ledande polymermembran som jon-till-elektronöverförare under en PVC-baserad jonselektiv membran. Sänkningen av detektionsgränsen åstadkoms med hjälp av koncentrations- och tidsbunden konditionering som återställde den jonselektiva elektrodens respons i ett koncentrationsområde ner till nanomol per liter. Denna konditioneringsmetod användes vid bestämningen av Pb^{2+} halter i syntetiska prov. Resultaten bekräftades med induktivt kopplad plasma-mass spektrometri (ICP-MS).

En förbättring av detektionsgränsen för Pb^{2+}-selektiva elektroder undersöktes också med fast-fas PbS/Ag_2S elektroder. Detektionsgränsen sänktes med hjälp av två metoder som minskade på parasitiska processer vid membranytan. Den första metoden bestod av en förbehandling av PbS/Ag_2S elektroden som resulterade i kontrollerad adsorption av analyten på elektrodytan (lägsta detektionsgränsen: ~ 10^{-8} mol dm^{-3} Pb^{2+}). Den andra metoden innebar en galvanostatisk polarisering av PbS/Ag_2S elektroden (lägsta detektionsgränsen: ~ 10^{-9} mol dm^{-3} Pb^{2+}). På grund av tidsbegränsningen för en enskild mätning som uppstod med den första metoden, användes den galvanostatiska polariseringsmetoden för mätningar av Pb^{2+} halter i såväl syntetiska som verkliga miljöprov. PbS/Ag_2S membranelektroder kunde framgångsrikt användas för kvantitativa bestämningar av bly(II)-halter i miljöprov, vilket bekräftades med andra analytiska metoder (ICP-MS och DPASV = differentiell puls anodisk stripping voltammetri). I denna avhandling presenteras nya metoder för att sänka detektionsgränsen för mätningar av låga och ultralåga analytkoncentrationer.

List of Publications

This thesis is based on the following papers, which are referred to in the text by their Roman numerals. The appended original publications are re-printed with the permission of the copyright holders.

I. G. Lisak, E. Grygolowicz-Pawlak, M. Mazurkiewicz, E. Malinowska, T. Sokalski, J. Bobacka, A. Lewenstam, *New polyacrylate-based lead(II) ion-selective electrodes*, **Microchim. Acta** 164 (**2009**) 293-297.

II. G. Lisak, M. Wagner, C. Kvarnström, J. Bobacka, A. Ivaska, A. Lewenstam, *Electrochemical behaviour of poly(benzopyrene) films doped with eriochrome black T as Pb^{2+}-sensitive sensors*, **Electroanalysis** 22 (**2010**) 2794-2800.

III. G. Lisak, J. Bobacka, A. Lewenstam, *Recovery of nanomolar detection limit of solid-contact lead(II) selective electrodes by electrode conditioning*, *In press*, **J. Solid State Electrochem**. (**2012**) DOI: 10.1007/s10008-012-1725-4.

IV. G. Lisak, T. Sokalski, J. Bobacka, L. Harju, A. Lewenstam, *A study on lowering the detection limit with solid-state lead-selective electrodes*, **Talanta** 83 (**2010**) 436-440.

V. G. Lisak, T. Sokalski, J. Bobacka, L. Harju, K. Mikhelson, A. Lewenstam, *Tuned galvanostatic polarization of solid-state lead-selective electrodes for lowering of the detection limit*, **Anal. Chim. Acta** 707 (**2011**) 1-6.

VI. G. Lisak, F. Ciepiela, J. Bobacka, T. Sokalski, L. Harju, A. Lewenstam, *Determination of lead(II) in ground water using solid-state lead(II) selective electrodes by tuned galvanostatic polarization* - submitted

Contribution of the Author:

Papers I, II, and VI. The author did the experimental work together with one of the co-authors, wrote the first draft of the manuscript, and finalized it in collaboration with the co-authors.

Papers III, IV and V. The author did the experimental work, wrote the first draft of the manuscript, and finalized it in collaboration with the co-authors.

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Abbreviations and symbols

$a_{\mathrm{Pb}^{2+}}^{\mathrm{sol}}, a_{\mathrm{Pb}^{2+}}^{\mathrm{mem}}$	activity of Pb^{2+} in solution and membrane ($\mathrm{mol\ dm}^{-3}$)
A	Debye-Hückel constant ($\mathrm{dm}^{3/2}\ \mathrm{mol}^{-1/2}$)
ACN	acetonitrile
AIBN	2,2-dimetoxy-2-phenylacetophenone
B	Debye-Hückel constant ($\mathrm{dm}^{3/2}\ \mathrm{mol}^{-1/2}\ \mathrm{nm}^{-1}$)
c_{i}	concentration ($\mathrm{mol\ dm}^{-3}$)
c_{std}	concentration of the standard solution ($\mathrm{mol\ dm}^{-3}$)
C	Debye-Hückel coefficient
DL	detection limit ($\mathrm{mol\ dm}^{-3}$)
E'	sinusoidal voltage (V)
E°	formal potential (V)
E_{cell}	potential of the potentiometric cell (V)
E_{d}	diffusion potential inside ion-selective membrane (V)
E_{er}	potential of external reference electrode (V)
E_{ir}	potential of internal reference electrode (V)
E_{j}	liquid junction potential (V)
E_{me}	potential at the membrane | sample interface (V)
E_{mi}	potential of the membrane | inner solution interface (V)
EbT	eriochrome black T
EMF	electromotive force (V)
f_{i}	activity coefficient for species i
F	Farday constant (96 485 $\mathrm{C\ mol}^{-1}$)
HDDA	1,6-hexanediol diacrylate
i	species i
i_{opt}	optimal current density ($\mathrm{nA\ cm}^{-2}$)
I	ionic strength
I'	sinusoidal current (A)
I_{c}	current (μA)
IDA	isododecyl acrylate
ISE	ion-selective electrode
ISM	ion-selective membrane
j	$\sqrt{-1}$ and interfering ion (when in index)
$K_{\mathrm{i}}^{\mathrm{pot}}$	potentiometric selectivity coefficient
$K_{\mathrm{iL}}^{\mathrm{i,L}}$	complexation constant
$K_{\mathrm{HL}}^{\mathrm{H,L}}$	protonation constant
K_{PbS}	unconditional solubility product of PbS
K'_{PbS}	conditional solubility product of PbS
LDL	low detection limit ($\mathrm{mol\ dm}^{-3}$)

mem	membrane
PBP	polybenzopyrene
PEDOT	poly(3,4-ethylenedioxythiophene)
PPy	polypyrrole
PVC	poly(vinyl chloride)
R	universal gas constant (8.314 J K^{-1} mol^{-1})
s	slope of the ion-selective electrode (mV dec^{-1})
S	solubility (mol dm^{-3})
sol	solution
SAM	single standard addition method
T	absolute temperature (K)
T_g	glass transition temperature (°C)
u_i	mobility of species i (cm^2 $V^{-1}s^{-1}$)
UDL	upper detection limit (mol dm^{-3})
V_i	volume (cm^3)
z_i	charge number of species i
z_+	charge number of cation
z_-	charge number of anion
Z	impedance (Ω)
α	reduction reactions
(α)	phase α
α_i	side reaction coefficient for species i
β	oxidation reactions
(β)	phase β
γ	adsorption of the main ion at the electrode surface
ϕ	phase angle
$\varphi^{\mathrm{sol}}, \varphi^{\mathrm{mem}}$	inner electric potential in solution and membrane (V)
$\mu^{\mathrm{sol}}_{\mathrm{Pb}^{2+}}, \mu^{\mathrm{mem}}_{\mathrm{Pb}^{2+}}$	chemical potential of Pb^{2+} in solution and membrane (J mol^{-1})
$\mu^{0,\mathrm{sol}}_{\mathrm{Pb}^{2+}}, \mu^{0,\mathrm{mem}}_{\mathrm{Pb}^{2+}}$	standard chemical potential of Pb^{2+} in solution and membrane (J mol^{-1})
$\tilde{\mu}^{\mathrm{sol}}_{\mathrm{Pb}^{2+}}, \tilde{\mu}^{\mathrm{mem}}_{\mathrm{Pb}^{2+}}$	electrochemical potential of Pb^{2+} in solution and membrane (J mol^{-1})

1. Introduction

In recent years there has been an increasing interest in the environmental sector of natural sciences as an increase in pollution in the environment has been observed. The industrial activity to sustain an ever growing human population leads to the uncontrolled release of pollutants. Currently the analysis of environmental samples is often undertaken by non-portable laboratory equipment such as inductively coupled plasma mass spectrometry (ICP-MS). This method, however, is an expensive, complicated and time consuming process. The need for a sensor that would operate preferably on site, with maintenance limited to a minimum and allowing relatively inexpensive mass production of the sensor, is the driving force for ongoing research [1, 2]. Therefore ion-selective electrodes (ISEs) are constantly investigated as candidates to replace already existing techniques in environmental analysis. Potentiometric sensors have several advantages over other analytical techniques such as portability, low energy consumption, and small size, which together provide an opportunity to perform analysis at an overall lower cost [3]. Although ICP-MS analysis of water pollutants may be applied successfully, total concentrations of water components are reported in comparison to concentrations of ionized forms obtained by ISEs. Due to this fact, information about the speciation of the ion in the sample may be obtained by using both ICP-MS and ISEs [4, 5].

As a result of the concern of the European Union as well as of the U.S. Environmental Protection Agency rigorous limits have been set for the maximum allowed concentration for each pollutant in the environment. The hazardous nature of many species requires constant monitoring of natural waters, soil and the atmosphere. In this work, there is a special concern about lead(II), its toxic nature in natural waters, and the potential methods to reliably determine the amount of lead in a variety of samples (including environmental samples). The method used to analyse Pb^{2+} in environmental samples was potentiometry, which is a powerful tool among electrochemical techniques. Since the restrictions on maximum lead content occurring in drinking water were set to be 15 ppb, a sensor which would operate in an extremely diluted solution is required [6, 7]. Ion-selective electrodes were recognized to be successfully applied in the determination of a great number of ions. However the possibilities of determining them at the submicro/nano-molar concentration range came with the concept of lowering of the detection limit of ion-selective electrodes [3]. The capability of measurements with ion-selective electrodes in a broad range of analyte concentration is clearly visible on a glass pH electrode. Covering the response from ca. pH 1 to 14, this electrode demonstrates possibilities for measurement with ion-selective electrodes under specific conditions including the architecture of the electrode [8-10]. Overall, many ISEs may operate in a broad analytical concentration range, and thus may be considered in ultra low analysis of analyte [3].

The detection limit has been an issue of interest since the early stages in the history of ISEs and initially solid-state membranes were under investigation. The possibility of lowering the detection limit for ISEs with plastic membranes was reported much later. It initiated an intensive and interesting research focused exclusively on plastic membranes. Solid-state membranes, although very successful as chemical sensors, are so far somewhat outside these trends. In particular, the possibilities for improvement of the detection limit of ion-selective electrodes (ISEs) with solid-state membranes have not been sufficiently explored [3].

The aim of this study is to obtain the design of the electrodes and possibilities of reliable measurements at low concentrations of Pb^{2+} ions. Those aspects are inspected by different methods to establish a practical protocol for lowering the detection limit for the determination of Pb^{2+} in environmental samples. To do this, wide spectrums of potentiometric sensors were applied. A conventional polymeric membrane electrode based on polyacrylates was investigated, and an all-solid sensor based on polybenzopyrene doped with eriochrome black T, both as a sensitive film and as a solid-contact with a polymeric PVC-based sensing membrane, was used. Finally, solid-state PbS/Ag_2S membrane electrodes for direct measurements of low concentrations of the main ion were re-examined. Novel approaches for Pb^{2+} analysis were developed and applied in the laboratory-based determination of lead(II) in environmental samples.

Although the theory of ion-selective electrodes is applicable for all ISEs, the working principles are primarily shown in the example of Pb^{2+}-ISE. All measurement protocols and methods of analysis were done for lead(II) selective electrodes (as representative). Finally, I express my sincere hope that this work will start a new trend in laboratory scale trace analysis of low and ultralow concentrations of pollutants in natural waters using ion-selective electrodes.

2. Principles and designs of potentiometric lead selective sensors

Potentiometry is one of the most commonly investigated and widely applied electroanalytical techniques. The attractiveness of this method is its relatively low cost compared to other analytical techniques, its portability, low energy consumption, the simplicity of the measuring system, and the possibility of miniaturization [3]. In traditional potentiometry, two electrode systems are used, consisting of an indicator, for example Pb^{2+}-selective electrode and a reference, for example double junction silver/silver chloride electrode (Figure 1).

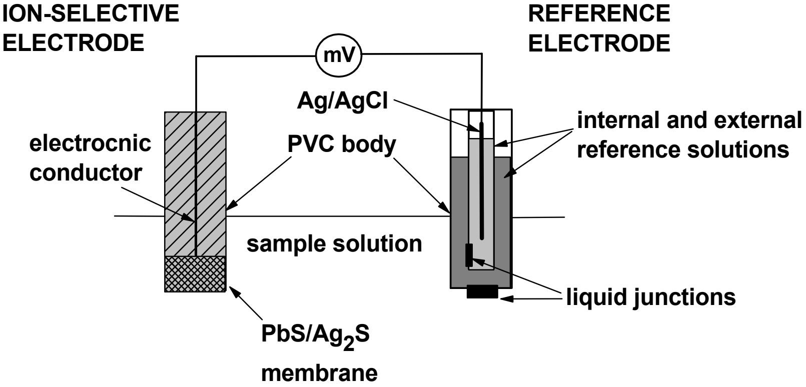

Figure 1. Schematic picture of potentiometric cell, as an example: Ag | AgCl | KCl (1 mol dm^{-3}) | KNO_3 (0.001 mol dm^{-3}) sample solution || PbS/Ag_2S solid-state electrode.

The electromotive force (*EMF*) is measured between the working and the reference electrode. In principle, the design of the reference electrode should assure a stable potential despite composition of the sample solution, so all changes of the *EMF* are attributed to the changes in potential of the ion-selective electrode. Potentiometric measurement is conducted at zero current conditions, where in a closed measuring circuit, a high input impedance (10^{13} Ω or higher) potentiometer is used [11-13]. Overall, the potentiometric cell may be considered as a galvanic cell, where the potential of the cell is the sum of various potential contributions [14, 15]. Generally, the potential of the cell with ion-selective electrode may be written as, eq. 1:

$$E_{\mathrm{cell}} = E_{\mathrm{er}} - E_{\mathrm{ir}} + E_{\mathrm{me}} - E_{\mathrm{mi}} + E_{\mathrm{d}} \pm E_{\mathrm{j}} \qquad (1)$$

where E_{er} is the potential of external reference electrode, E_{ir} is the potential of internal reference electrode, E_{me} is the potential at the membrane | sample interface, E_{mi} is the potential of the membrane | inner solution interface, E_{d} is a diffusion potential inside ion selective membrane and E_{j} is liquid junction potential.

The potential of the potentiometric cell is simplified due to the constant potential contributions coming from the phase boundary potential of the solid-contact | membrane interface (solid-state and solid-contact Pb^{2+}-ISEs) and inner ion-selective electrode solution | membrane interface (conventional Pb^{2+}-ISEs), as well as potentials of internal and external reference electrodes which remain constant during the measurements and independent of the sample composition. The diffusion potential inside the membrane is neglected, often considered to be zero. However ion gradients may occur when various ions with different mobilities are present inside the ion-selective membrane and in this case the contribution of diffusion potential may be significant, for example membranes with induced transmembrane ion fluxes for lowering of the detection limit. The main contribution to the overall cell potential comes from the phase boundary potential of the membrane | sample interface and the liquid junction potential (diffusion potential in conventional reference electrodes) [13, 14]. The recognition process of ions by ion-selective electrode occurs at the membrane | sample interface, where a space charge region is formed at the surface of the membrane. A potential layer arises from the charge separation of the primary (Pb^{2+}) and counter ion, where Pb^{2+} is by chemisorption attracted to the surface of the membrane while counter ion accumulates in the sample solution [16-18]. Furthermore, whenever two solutions with various compositions are in contact with each other, for example separated with permeable membrane, diffusion potential occurs. It originates from the gradient of chemical potentials for each component of solutions on both side of the membrane [19]. As a result of the charge separation, potential difference will be created in the liquid junction due to various mobilities of the ionic species. The junction potential however can be kept rather small or constant and moreover may be estimated using the Henderson equation assuming that the ion concentrations are equal to their activities and that the concentration profiles are linear throughout the junction, eq. 2 [20, 21]:

$$E_\mathrm{j} = \frac{\sum_\mathrm{i} \frac{|z_\mathrm{i}| u_\mathrm{i}}{z_\mathrm{i}} [c_\mathrm{i}(\beta) - c_\mathrm{i}(\alpha)]}{\sum_\mathrm{i} |z_\mathrm{i}| u_\mathrm{i} [c_\mathrm{i}(\beta) - c_\mathrm{i}(\alpha)]} \frac{RT}{F} \ln \frac{\sum_\mathrm{i} |z_\mathrm{i}| u_\mathrm{i} c_\mathrm{i}(\alpha)}{\sum_\mathrm{i} |z_\mathrm{i}| u_\mathrm{i} c_\mathrm{i}(\beta)} \qquad (2)$$

where, z_i is the charge number, u_i is the mobility and c_i is molar concentration of species i, (α) and (β) are the two phases meeting each other, R is the universal gas constant, T is the absolute temperature and F is Faraday constant.

The conventional type of the reference electrode has an inner reference solution which via a porous glass frit or a ceramic plug is put in contact with sample solution, allowing contact but not the mechanical mixing of the two solutions [22]. For many applications a single junction reference electrode is enough to perform a successful determination of ions. It requires highly concentrated reference solution. To minimize undesired effects, for example the influence of diffusion potential and/or contamination of sample with leaking highly concentrated reference solution, the double junction electrodes equipped with electrolytes of approximately the same ion mobilities are used [23]. This modification of the reference electrode is truly significant for the determination of ultra low concentrations of Pb^{2+}.

A commonly accepted mechanism of the response of the ion-selective electrode is based on the phase boundary potential model. Lead(II) ions can effectively interact in a selective manner with vacancies (unoccupied places) in the crystalline structure of, for example PbS/Ag_2S membrane in solid-state electrodes, with ionophore, with a complexing agent, with the functionalized polymeric material in plastic membranes, and with polymeric films when used as sensing membranes. The activities of Pb^{2+} in the membrane and in the sample solution are in equilibrium, determined by equal electrochemical potential in each of the phases. Due to electroneutrality reasons no net current may flow in the system. Thus, only main ion (analyte) when transferred between membrane and sample solution phases carries charge which result in interfacial charge separation at the phase boundary [3, 24, 25]. From the phase boundary potential model the response of Pb^{2+}-ISE may be derived as follows.

Since the local equilibrium is established at the membrane | sample solution interface the electrochemical potential for Pb^{2+} in the sample solution is equal to the electrochemical potential of Pb^{2+} in the membrane ($\tilde{\mu}^{\mathrm{sol}}_{\mathrm{Pb}^{2+}} = \tilde{\mu}^{\mathrm{mem}}_{\mathrm{Pb}^{2+}}$) and the equation may be expressed as, eq. 3:

$$\mu^{0,\mathrm{sol}}_{\mathrm{Pb}^{2+}} + RT\ln(a^{\mathrm{sol}}_{\mathrm{Pb}^{2+}}) + z_{\mathrm{Pb}^{2+}}F\varphi^{\mathrm{sol}} = \mu^{0,\mathrm{mem}}_{\mathrm{Pb}^{2+}} + RT\ln(a^{\mathrm{mem}}_{\mathrm{Pb}^{2+}}) + z_{\mathrm{Pb}^{2+}}F\varphi^{\mathrm{mem}} \qquad (3)$$

where $\tilde{\mu}^{\mathrm{i}}_{\mathrm{Pb}^{2+}}$ is the electrochemical potential, $\mu^{0,\mathrm{i}}_{\mathrm{Pb}^{2+}}$ is the standard chemical potential, $z_{\mathrm{Pb}^{2+}}$ is charge number for Pb^{2+} ($z_{\mathrm{Pb}^{2+}} = +2$), $a^{\mathrm{i}}_{\mathrm{Pb}^{2+}}$ is the activity of Pb^{2+}, φ^{i} is the inner electric potential, and R,T and F have already been explained. Upper index refers to two phases: "sol" sample solution, "mem" ion selective membrane.

The response of Pb^{2+}-ISE is then defined as a contribution of chemical potential and electric work of Pb^{2+} in sample solution and in the membrane. Finally, the electric potential of such system is defined as, eq. 4:

$$E^{\mathrm{pot}}_{\mathrm{Pb}^{2+}} = \Delta\varphi = \varphi^{\mathrm{mem}} - \varphi^{\mathrm{sol}} = \frac{\mu^{0,\mathrm{sol}}_{\mathrm{Pb}^{2+}} - \mu^{0,\mathrm{mem}}_{\mathrm{Pb}^{2+}}}{z_{\mathrm{Pb}^{2+}}F} + \frac{RT}{z_{\mathrm{Pb}^{2+}}F}\ln\frac{a^{\mathrm{sol}}_{\mathrm{Pb}^{2+}}}{a^{\mathrm{mem}}_{\mathrm{Pb}^{2+}}} \qquad (4)$$

Assuming that $\mu^{0,\mathrm{sol}}_{\mathrm{Pb}^{2+}}, \mu^{0,\mathrm{mem}}_{\mathrm{Pb}^{2+}}, z_{\mathrm{Pb}^{2+}}, F$, and $a^{\mathrm{mem}}_{\mathrm{Pb}^{2+}}$ are constant they may be included in the constant $E^{0}_{\mathrm{Pb}^{2+}}$ (formal potential of the Pb^{2+}-ISE) and when no interferences from other ions are considered, the final equation for the response of Pb^{2+}-ISE is described by **Nernst equation**, eq. 5:

$$E^{\mathrm{pot}}_{\mathrm{Pb}^{2+}} = E^{0}_{\mathrm{Pb}^{2+}} + \frac{RT}{z_{\mathrm{Pb}^{2+}}F} \ln a^{\mathrm{sol}}_{\mathrm{Pb}^{2+}} \tag{5}$$

The Nernst equation is the most fundamental formulation in potentiometry and describes the relation between the potential of the indicator electrode and the activity of the analyte. For a lead(II) selective electrode the potential is directly proportional to the changes of the activity ($\log a_{\mathrm{Pb}^{2+}}$) when reformulating eq.5, as it is shown in eq. 6:

$$E^{\mathrm{pot}}_{\mathrm{Pb}^{2+}} = E^{0}_{\mathrm{Pb}^{2+}} + \frac{0.059\mathrm{V}}{z_{\mathrm{Pb}^{2+}}} \log a^{\mathrm{sol}}_{\mathrm{Pb}^{2+}} \tag{6}$$

The factor $\frac{0.059\mathrm{V}}{z_{\mathrm{Pb}^{2+}}}$ is the slope of the $E^{\mathrm{pot}}_{\mathrm{Pb}^{2+}} = \mathrm{f}(\log a^{\mathrm{sol}}_{\mathrm{Pb}^{2+}})$ curve for the Pb^{2+}-ISE. Theoretically, for Pb^{2+}-selective electrode, the slope is equal to 29.6 mV (25°C) for the tenfold change in Pb^{2+} activity.

Ion-selective electrodes are called “selective”, a term which indicates that each electrode response is dictated selectively by the primary ion, for which the electrode was designed for, in presence of other interfering ions. To describe the response of the Pb^{2+}-ISE in presence of interfering ions (including the factor of selectivity) an extended Nernst equation (eq. 5), the Nikolskii-Eisenman equation may be provided, eq. 7:

$$E^{\mathrm{pot}}_{\mathrm{Pb}^{2+}} = E^{0'}_{\mathrm{Pb}^{2+}} + \frac{RT}{z_{\mathrm{Pb}^{2+}}F} \ln\Big(a^{\mathrm{sol}}_{\mathrm{Pb}^{2+}} + \sum_{\mathrm{Pb}^{2+} \neq \mathrm{j}}^{\mathrm{j}} K^{\mathrm{pot}}_{\mathrm{Pb}^{2+},\mathrm{j}} a_j^{\frac{z_{\mathrm{Pb}^{2+}}}{z_{\mathrm{j}}}}\Big) \tag{7}$$

where, $E^{0'}_{\mathrm{Pb}^{2+}}$ is the formal potential of Pb^{2+}-ISE including junction potential, $K^{\mathrm{pot}}_{\mathrm{Pb}^{2+},\mathrm{j}}$ is selectivity coefficient for lead over interfering ion (for example j= Cu^{2+}, Zn^{2+}, Cd^{2+}, …)

Selectivity coefficient is the factor which describes the influence of various interfering ions on ISEs. Much effort is put into investigating the origin of the selectivity of various ISEs and its dependence on the type of material from which the electrode is built and/or continuous search for active components (ionophores) with high selectivity toward specific ions [26]. For lead(II)-selective electrodes various materials have been tested as active components of the membrane for highly selective measurements of lead(II) in environmental samples [27-29]. A constant search for a reliable sensor for Pb^{2+} analysis led to a variety of designs of Pb^{2+}-ISEs. Four significant groups of electrodes are shown in Figure 2.

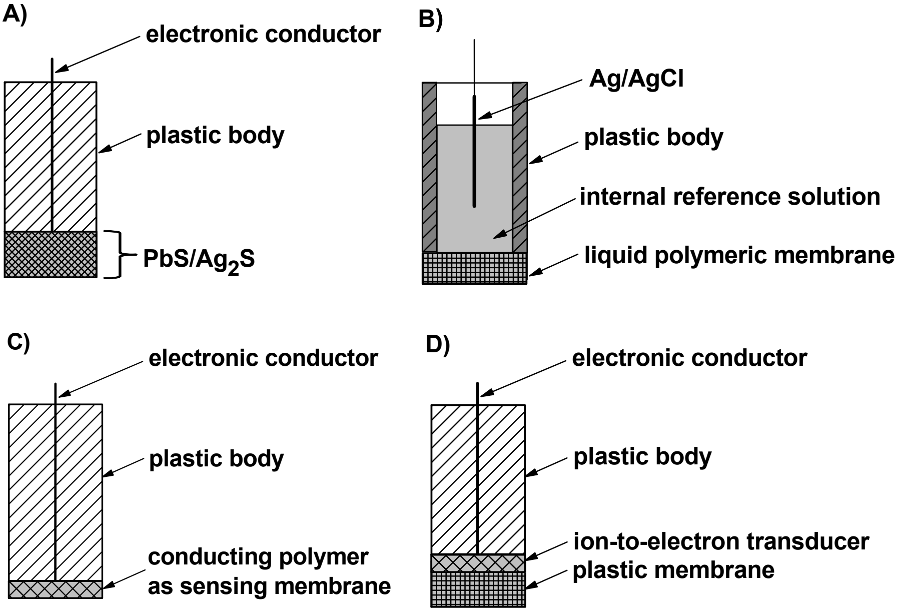

Figure 2. Various types of Pb^{2+}-ISE electrodes: A) solid-state based on sparingly soluble salts, for example PbS/Ag_2S, B) conventional with liquid polymeric membrane, C) conducting polymer film as sensing membrane, and D) solid-contact with polymeric membrane.

The general design of solid-state membranes is based on sparingly soluble salts. Various designs of solid-state lead selective electrodes were developed, for example PbS, PbSe, PbTe with Ag_2S as a filling material that increases the conductivity, or more sophisticated designs such as PbS/As_2S_3, $PbS/Ag_2S/As_2S_3$ or $PbI_2/Ag_2S/As_2S_3$ [30-33]. However the most investigated, and in consequence the most commercialized, have been solid-state lead-selective electrodes based on PbS/Ag_2S membranes [34].

Typically the conventional type of Pb^{2+}-ISEs is based on an Ag/AgCl inner electrode, inner reference solution (usually containing primary ion and/or chloride salt) and a plastic membrane. The polymeric membrane is based on water-immiscible substances. Vast majority of membranes are based on poly(vinyl chloride) (PVC) in which ionophores (primary ion binding sites), plasticizers to improve physical properties, for example to lower glass transition temperature to obtain better flexibility of the membranes, and ionic additives (to avoid interferences from counter ions, thus the permselectivity of the membrane is ensured) are embedded [14, 35, 36]. Additionally, methacrylic/acrylic-based membranes instead of PVC-based membranes were developed to significantly decrease the glass transition temperature, thereby obtaining plasticizer-free membranes [37-41]. Finally, the success of conventional Pb^{2+}-ISEs led to commercialization of highly selective lead(II)-selective ionophores [42-44].

Conducting polymers (CPs) have been used to replace inner reference solution of conventional Pb^{2+}-ISEs. As a result all-solid state types of sensors were developed. Ion-to-electron transduction was obtained due to the application of conducting polymer film on to the electronic conductor surface, thereby allowing the smooth transfer of signal from ions in the solution to the electronic conductor [45, 46]. Among other membranes, derivatives of polypyrrole, polyaniline, and polythiophene-based membranes were developed and studied [47]. Such conducting polymers were applied in ion-selective electrodes as a sensing membrane and as a solid contact material between ISM and electronic conductor (solid-contact ISEs). For conducting polymers used as ion-selective films, the sensing mechanism is driven by the interactions of analyte with functional groups on the conducting polymer backbone or a doping ion used for electropolymerization (often exhibiting complexation properties with primary ion) [48-50]. The analytical use of such system is limited, however, due to unselective ionic response of the conducting polymer film. To avoid this problem CPs were mostly used as ion-to-electron transducers, while the polymeric membrane was responsible for sufficiently selective binding of the analyte. Though thiol-based self-assembled monolayers were considered as ion-to-electron transducers, the properties and the simplicity of the electropolymerization led to the application of CPs as a common contact material [51]. Introduction of CPs to the architecture of Pb^{2+}-ISEs created the possibility of miniaturization, of lowering of the detection limit, improved stability of the response and a prolonged lifetime for the electrodes [52-54].

3. Lead in the environment

Lead *(Latin: plumbum)* is a heavy metal naturally occurring in the environment. Lead is rarely present in metallic form. The most abundant form of lead ore is called galena (PbS). Other forms such as cerrusite ($PbCO_3$) and anglesite ($PbSO_4$) are present in smaller quantities; thus for industrial use galena is the most relevant lead ore. Typically, lead-rich minerals occur together with other metals, such as silver, copper and zinc. It has been estimated that the lead-orientated industry worldwide is worth billions of dollars. The first existence of a lead product has been dated to 4000 BC (in a lead figurine found in Egypt). Nowadays, galena is used to obtain lead-based products of which the most commonly known are lead-acid batteries, cathode ray tubes, pigments, alloys, polymer additives, ammunition, glasses and glazes, cable sheathing and radiation screening materials [55].

Galena undergoes oxidation in an aqueous environment to a variety of species, according to the pH and electrochemical state of the system [56-58]. The proposed oxidation of sulphide from galena resulting in a release of Pb^{2+} is shown in eq. 8 [59, 60]:

$$\mathrm{PbS} + \frac{1}{2}\mathrm{O_2} + 2\mathrm{H^+} \rightarrow \mathrm{Pb^{2+}} + \mathrm{S} + \mathrm{H_2O} \qquad (8)$$

Additionally, sulphide may also be oxidized by bacterial activity [61]. Lead is naturally present in low concentrations (2 to 200 μg dm^{-3}) in soils, rocks and dusts. The concentration of lead in waters is estimated to be even lower. The oxidation of PbS in aqueous media result in the release of Pb^{2+}, so due to environmental activities (blown rich-lead dust), the concentration of lead in some natural waters may be above average. However the principal cause of lead pollution is industrial activity. Mining, smelting and refining of lead produces huge quantities of lead-rich dust which contaminates vast areas surrounding industrially active places. The level of lead in the blood of workers and their families from lead-related industrial sites are as a rule higher than for other people [55, 62-64]. Moreover, past activity such as the use of leaded petrol or leaded paint caused a significant increase in total free lead concentration in the environment. Exposure to lead by ingestion (drinking lead-rich water or eating lead-rich vegetables, fruits and animal products), inhalation and dermal contact (mostly with lead-rich dust) can cause significant toxicity. In a daily diet, approximately 300 μg of lead is consumed. Children's health is of greater concern as they absorb up to 50%, while for adults it was estimated to be approximately 10% of a daily in-take. A significant part of absorbed lead is further implicated in the biological cycle [55, 65, 66]. Lead(II) inhibits amino levulinic acid dehydratase (ALAD) which catalyses the synthesis of heme from porphyrin. Furthermore, due to the lack of heme, anaemia is frequently observed. Blood analysis has the strongest correlation with lead toxicity. For example as an indication 10 μg in 0.1 dm^{-3} whole blood lead level for children is considered as standard. However even smaller lead concentration may affect growth and hearing in children. A concentration of whole blood lead higher than 30 μg in 0.1 dm^{-3} is considered potentially dangerous, indicating significant lead exposure resulting in higher blood pressure and a decrease in vitamin D metabolism. A level of 60 μg in 0.1 dm^{-3} whole blood lead is considered hazardous for human health causing lead poisoning (*plumbism*) with anaemia, abnormal pain, and in more serious cases, resulting in coma. As a result of this abnormal level of lead in the whole blood chelation therapy must be performed. Lead can in fact pose a mortal threat to human health since high whole blood lead concentration (above 120 μg in 0.1 dm^{-3}) is potentially fatal [55, 67, 68].

4. Detection limits of ISEs

The specific response of every ion-selective electrode to the analyte is limited by the consecutive parameters of all ion-selective electrodes selectivity and by the detection limit (*DL*) [3]. Consequently the response of the ion-selective electrode is limited by an upper (*UDL*) and a lower (*LDL*) detection limit, and the analytical importance of ISEs is then defined in between those two detection limits.

Finally, the response of Pb^{2+}-ISE should be Nernstian and governed by the Nikolskii-Eisenman equation (eq. 7) enriched by the parameter of the detection limit, eq. 9:

$$E^{\mathrm{pot}}_{\mathrm{Pb}^{2+}} = E^{0'}_{\mathrm{Pb}^{2+}} + \frac{RT}{z_{\mathrm{Pb}^{2+}}F}\ln(a^{\mathrm{sol}}_{\mathrm{Pb}^{2+}} + \sum_{\mathrm{Pb}^{2+}\neq \mathrm{j}}^{\mathrm{j}} K^{\mathrm{pot}}_{\mathrm{Pb}^{2+},\mathrm{j}} a_j^{\frac{z_{\mathrm{Pb}^{2+}}}{z_{\mathrm{j}}}} + DL) \qquad (9)$$

The definition of the detection limit for ion-selective electrodes is different from other analytical techniques. Instead of three times the standard deviation of the background noise it is defined by IUPAC as a cross section of the two linear parts of calibration curve (Nernstian and non-Nernstian) [69,70]. Schematically it is shown in Figure 3 A where the upper and lower detection limits are marked on the calibration curves for a Pb^{2+}-ISE.

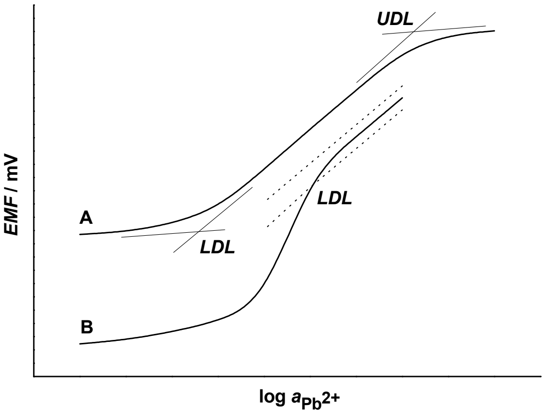

Figure 3. Calibration curve of Pb^{2+}-ISE with upper (*UDL*) and lower (*LDL*) detection limits marked: A) Detection limits according to IUPAC, B) Detection limit in the case of super-Nernstian response, proposed by T. Sokalski et al. [71].

However from new findings on lowering the detection limit for polymeric membrane electrodes, it was proposed that *LDL* should be defined as a deviation of the *EMF* response by $RT/z_{\mathrm{Pb}^{2+}}F\ln 2$ from the extrapolated linear (Nernstian) part of the calibration curve (presented in Figure 3 B) [71]. This approach was proposed mostly for electrodes with a super-Nernstian response, since the IUPAC definition has no applicability in that case. Indeed the upper detection limit may be described by either approach as the mathematical meaning for both is roughly the same.

The upper detection limit is governed by the coextraction of primary ion and counter ions from the sample solution to the ion-selective membrane with an increase in sample concentration. This process leads to a loss of permselectivity of the membrane (Donnan failure) which means that for a Pb^{2+} sensitive membrane only cations will be able to enter the membrane, leaving all anions in the solution [72, 73]. The upper detection limit, thus the degree of coextraction, ultimately depends on the complexing strength of the ionophore and the amount of counter ionic sites, for example lipophilic salt, in the membrane.

From environmental analysis, such as trace analysis of pollutants, the lower detection limit is of a much greater importance than the upper detection limit. In potentiometric solid-state sensors based on a crystalline membrane, the detection limit is governed by the conditional solubility product of membrane components, defined by the parasitic processes at the solid-state surface. For plastic membrane sensors the lower detection limit is highly influenced by the zero-current fluxes of ions inside ion-selective membranes and insufficient selectivity to the primary ion over interfering ions [74-76]. Usually the detection limit of most ion-selective electrodes is approximately 10^{-6}-10^{-7} mol dm^{-3} for Pb^{2+}-ISEs, so the modification of the electrode design and the adjustment of the measurement procedures and techniques must be undertaken to measure reliably at even lower lead(II) concentrations. The issue of measurements in extremely diluted sample solutions by ISEs will be discussed further in the subsequent chapter.

5. Lowering of the detection limit

5.1 *LDL* of solid-state electrodes

The first works concerning the lowering of the detection limit were devoted to solid-state membranes [74, 77, 78]. Ideally the solubility product of the membrane's components determines the possibility of lowering the detection limit [79-84]. For PbS/Ag_2S membrane the detection limit dictated by the thermodynamic unconditional solubility product of PbS is equal to $10^{-13.3}$ mol dm^{-3} Pb^{2+} [85].

Unfortunately there are a number of side effects that hinder the electrode response in diluted samples in direct measurements without ionic buffers. One of the most important side effects is oxidation/reduction of the membrane components entailing release of the analyte ion from the membrane material into the sample in the vicinity of the membrane/solution interface. Adsorption of analyte on the membrane surface and/or container walls, followed by desorption when in contact with a more diluted solution may also result in large deviations from a Nernstian response, especially in unsupported samples. Interference from impurities may also increase with dilution. Because of these side effects the detection limit of solid-state membranes in direct measurement is usually not lower than 10^{-6}-10^{-7} mol dm^{-3} Pb^{2+}. It was shown that in unbuffered media such ions as fluoride, chloride, iodide and sulphide can be readily measured down to 10^{-7} mol dm^{-3} [78, 86-91].

A simple but effective illustration of possibilities of lowering the detection limit of solid-state electrodes was demonstrated with measurements in well-controlled conditions. Indeed, low detection limit dictated by the thermodynamic solubility product was observed for numerous solid-state membrane ISEs in purposely supported systems, for example in ionic buffers and in titrations, where the activity of the main (primary) ion is controlled by complexation and/or solubility reactions [92]. For solid-state PbS/Ag_2S, the application of ionic buffers exhibited close to a Nernstian response in the dynamic range of pPb^{2+} 2 to 11 resulting in detection limit nearby the one dictated by thermodynamic unconditional solubility product of PbS [93]. When side reactions and parasitic processes (including interference from other ions) are marginalized, the detection limit is improved. In consequence, the Nernstian response of the electrode may be extended to the extremely low concentration range [77, 87, 94]. The method concludes that even small amounts of interfering species drastically worsen the low detection limit of ion-selective electrodes in unbuffered conditions [93]. On the other hand it strongly indicates that eliminating interferences by performing measurements under well-controlled conditions (buffered solutions with constant pH) makes the response of solid-state lead-selective electrodes closer to the theoretical value of the low detection limit. This method is limited, however, in practical applications, and was usually applied to inspect the dynamic range of the electrode under controlled conditions.

More practical ways of lowering the detection limit of the solid-state ion-selective electrodes may be carried out in various ways. One approach is to eliminate all interferences in unbuffered solutions by a well-established preparation and measurement protocol, for example high purity of chemicals, suitable type of containers, renewal of electrode surface, cleaning procedure of working and reference electrodes. In this way the uncertainties of the measurement are minimized, resulting in more reproducible readouts in diluted samples. This approach, however, does not allow the elimination of the intrinsic obstacles like oxidation/reduction of the membrane components and therefore provides only minor improvement of the detection limit. In addition to the factors influencing solubility product, the bias from interfering ions, uncontrolled interference from supporting electrolyte, the adsorption of primary ions on the wall of the measuring containers, or non-controlled impurities could significantly affect the low detection limit [78, 85, 95, 96].

Decreasing the side reactions of the membrane components, and thereby lowering the release of the primary ion into the sample solution, appears to be the most important step in reaching the thermodynamic detection limit. Therefore numerous parameters need to be considered when a solid-state ISE is used at concentrations close to the detection limit. In the absence of interfering ions, the potential of the ISE is depicted by the following semiempirical equation (eq. 10) valid for solid-state membrane ISEs [78, 97]:

$$E = E^0 + \frac{RT}{z_\mathrm{i}F}\ln\frac{1}{2}\left[\left(a_\mathrm{i}^{\mathrm{A}} + \beta - \alpha + \gamma\right) + \left[\left(a_\mathrm{i}^{\mathrm{A}} + \beta - \alpha + \gamma\right)^2 + 4Kso\right]^{1/2}\right] \qquad (10)$$

where $a_\mathrm{i}^{\mathrm{A}}$ is a free main ion activity; β is oxidation and α is reduction reactions that liberate and consume the main ion; γ is adsorption of the main ion at the electrode surface; and Kso is the thermodynamic solubility product; z_i is the charge of the main ion; T is temperature in °K; R is the gas; and F is the Faraday constants.

In the absence of parasitic effects ($\alpha, \beta, \gamma = 0$), the detection limit is governed exclusively by the solubility product. It was expected, and was observed before, that adsorption of the main ion, γ, is concentration and time dependent, and so is the potential of the solid-membrane ISE, if adsorption predominates [78]. For the lead sulphide electrode it was concluded that the Pb^{2+} is involved in physi- and/or chemi-sorption onto the solid-state surface. To deal with that problem a mechanical or a chemical etching of the surface was applied [98]. To reduce problems with the adsorption processes, vigorous stirring and polishing of the electrode surface might also be applied. However in most cases adsorption on the membrane surface cannot be entirely eliminated [78, 96, 99, 100].

If solubility is increased by side reactions, the actual solubility should be calculated from the conditional solubility product as shown below [78, 101]. When considering the PbS/Ag_2S solid-state electrode, the following equation is valid for the conditional solubility product, K'_{PbS} of lead sulphide, eq. 11:

$$K'_{\mathrm{PbS}} = K_{\mathrm{PbS}}\alpha_{\mathrm{Pb(OH,X)}}\alpha_{\mathrm{S(H)}} \tag{11}$$

where K_{PbS} is thermodynamic (unconditional) solubility product of the reaction, eq. 12:

$$\mathrm{PbS} \rightleftharpoons \mathrm{Pb}^{2+} + \mathrm{S}^{2-} \tag{12}$$

while $\alpha_{\mathrm{Pb(OH,X)}}$ and $\alpha_{\mathrm{S(H)}}$ are side reaction coefficients, which depend on the extent of complex formation processes.

Without considering side-reactions $\alpha_{\mathrm{Pb(OH,X)}} = \alpha_{\mathrm{S(H)}} = 1$ and the activity of lead ions resulting from membrane dissolution is, eq. 13:

$$[\mathrm{Pb}^{2+}] = \sqrt{K_{\mathrm{PbS}}} \sim 10^{-13.3} \tag{13}$$

Due to side-reactions of lead ions, for example complex formation with X^- and/or OH^- ions and sulfide ions, for example protonation of S^{2-}, side reaction coefficients in the system are greater than one; $\alpha_{\mathrm{Pb(OH,X)}}$ and $\alpha_{\mathrm{S(H)}} > 1$. For such a case the conditional solubility product K'_{PbS} is used for the calculation of the real solubility of PbS according to Ringbom [85], eq. 14 and eq. 15:

$$\alpha_{\mathrm{Pb(OH,X)}} = 1 + \left[\mathrm{OH}^-\right]K_{\mathrm{Pb(OH)}} + \left[\mathrm{OH}^-\right]^2 K_{\mathrm{Pb(OH)_2}} + \left[\mathrm{X}^-\right]K_{\mathrm{Pb(X)}} + \left[\mathrm{X}^-\right]^2 K_{\mathrm{Pb(X)_2}} \tag{14}$$

$$\alpha_{\mathrm{S(H)}} = 1 + \left[\mathrm{H}^+\right]K_{\mathrm{HS}} + \left[\mathrm{H}^+\right]^2 K_{\mathrm{H_2S}} \tag{15}$$

where K are respective stability constants for indexed species.

The conditional solubility product allows calculating free lead ion activity due to membrane dissolution by the following equation, eq. 16:

$$[\mathrm{Pb}^{2+}] = \sqrt{\frac{K'_{\mathrm{PbS}}}{(\alpha_{\mathrm{Pb(OH,X)}})^2}} = \sqrt{\frac{K_{\mathrm{PbS}}\alpha_{\mathrm{S(H)}}}{(\alpha_{\mathrm{Pb(OH,X)}})}} \qquad (16)$$

The predominant side reactions of PbS are caused by the solution pH. Due to side reactions, for example protonation and parasitic processes, oxidative dissolution or adsorption, the experimentally observed solubility is, as a rule, higher than that expected based on the thermodynamic solubility product. In consequence, by lowering/eliminating the redox and adsorption processes on the surface of the membrane (decreasing redox potential by, for example the addition of ascorbic acid and removing dissolved oxygen from the sample solution by purging with inert gas) a lowering of the detection limit of solid-state membrane can be obtained [80-82, 102, 103].

Another approach to decrease *LDL* is to apply ISEs in current controlled measurements. The first works concerning direct current interaction with solid-state membranes were devoted to glass electrodes. It was discovered that small currents passed through the ISE create differences in electrode potential. Once the current was switched off, the potential value of the electrode returned gradually to the potential at zero current conditions [104, 105]. Subsequently measurements were performed with membranes based on sparingly soluble salts. Influences of both cathodic and anodic polarization were investigated [106]. However, the primary use of applying current to solid-state membranes was to obtain less uncertainty during titrations rather than a lowering of the detection limit [107].

5.2 *LDL* of plastic membrane electrodes

The design of plastic membrane electrodes dates back to the 1960s. By incorporating active substances (crystals, ion-exchangers, neutral carriers) to the polymeric membranes the measurements of ion activities became possible. Finally, to obtain sufficient selectivity and sensitivity, additional components (lipophilic salts, plasticizer) were added to the polymeric membrane [35, 108-111]. Although novel, highly-selective ionophores were discovered and tested, the detection limit of polymeric membranes in comparison to solid-state membranes was still similar, around 10^{-6}-10^{-7} mol dm^{-3} [27, 112-115].

In the conventional type of ISEs, the ion-selective membrane is in contact with the sample solution and the inner reference solution. It was convincingly documented that the inner reference solution plays a crucial role in the overall response of ISEs, as a result of transmembrane ion fluxes [116]. This response is even more pronounced in diluted solutions as the flux of primary ion from the inner compartment of the ISE to the sample solution results in much higher activity of primary ion at the membrane | sample solution interface than in the bulk of the sample solution. This contamination of the ISM surface with the main ion is a primary cause of worsening of the detection limit, as it limits the electrode in measurements at extremely low activities. Consequently, the possibilities of lowering of the detection limit of polymeric membrane ion-selective electrodes were mostly concentrated on adjusting ion fluxes through the ISM [116-118].

Pioneering works on lowering of the detection limit of conventional ISEs were devoted to the implementation of the inner reference solution with extremely low activity of primary ion, often in picomolar activity range. With Pb^{2+}-ISEs, a tremendous improvement in the detection limit was possible by inducing the flux of primary ion from the sample solution to the inner reference solution, creating a so-called "ion uptake effect" [71, 119]. This effect is attributed to the activity of the analyte at the membrane | sample solution interface which is depleted due to the faster uptake of ions inside the membrane than when transported from the bulk of the solution to the membrane surface for conventional ISEs with low activity of the primary ion in the inner reference solution and/or unconditioned membranes. Thus, the lowering of the detection limit was only possible with well optimized composition of the inner reference solution; otherwise a super-Nernstian response was recorded [120]. Therefore, much study was devoted to optimizing the composition of the inner solution as well as the thickness of the ion selective membrane for lowering of the detection limit [120-124]. Furthermore, changing the composition of the membrane itself results in the decrease of transmembrane ion fluxes. This was realized by applying various polymeric material-plasticizer ratios, as well as decreasing the quantity of ion-exchanger in the ion-selective membrane [123]. Other ways to deal with ion fluxes in the membrane were to bind covalently the ionophore to the polymer backbone to diminish leaching of active components from the polymer matrix or to introduce material other than polyvinyl chloride (PVC) with lower ion diffusion coefficients inside the membrane, for example derivatives of polyacrylates [125-127]. Transmembrane ion fluxes can also be eliminated by galvanostatic polarization of the ion selective membrane. By applying a controlled current, an electric field is induced which reduces the gradient of the electrochemical potential of the analyte across the membrane, and in this way reduces the transmembrane flux. This method is a promising tool for lowering the detection limit with ISEs [128-137]. Above all, for polymeric membranes a mathematical model was introduced to predict and illustrate the detection limit under various conditions. Thus by applying the Nernst-Planck-Poisson model it was shown that the detection limit of ISEs is concentration and time dependent. In principle, an improved low detection limit could be obtained by taking advantage of transmembrane ion fluxes by applying an appropriate composition of inner filling solution and potential readout time [97, 138].

The applicability of conventional ISEs with inner reference solution is limited due to problems with miniaturization and a constant evaporation or/and leaching of the reference solution. Consequently, all-solid state type of ISEs were developed and further applied in the lowering of the detection limit. The Ag/AgCl | inner reference solution of the conventional type of ISEs was deliberately replaced with another type of material which would similarly act as transducer transferring the signal from the ion-selective membrane to the electronic conductor. This allowed miniaturization and less maintenance than with conventional type of ISEs. A conducting polymer may be used as ion-selective membranes in which the response to the analyte ultimately depends on complexation constants of immobilized metal-complexing ligands that retained complexation properties inside the conducting polymer films [139-143]. Typically, the complexation is not selective enough for a particular ion so these types of all-solid state sensors exhibit detection limits not lower than 10^{-5}-10^{-6} mol dm^{-3} [144-146]. Together with possible spontaneous charging and discharging of CPs, with sensitivity to light, the pH and dissolved gases, a lowering of the detection limit of this kind of sensor is limited [147-150].

More promising in lowering of the detection limit are solid-contact ISEs [3, 45-47, 54, 151-156]. The solid-contact design may significantly help in lowering transmambrane ion fluxes as it replaces the inner reservoir of highly concentrated solution (conventional ISEs) with a solid-contact conducting polymer layer. Additionally, conducting polymer film may be doped with a compound which complexes the primary ion, thus promoting a supplementary driving force for it to enter the membrane [157, 158].

Since solid-contact electrodes may deteriorate, however, during a long period of use, some improvements in the detection limit were obtained in well-controlled (measurement protocol), well-established (obtaining solid-contact electrodes) conditions for disposable screen-printed electrodes. Additionally, the conventional reference electrode may also be a source of contaminating ions, thereby inducing significant junction potential or not allowing miniaturization. Thus, disposable potentiometric ion sensors based on solid-contact ISEs combined with solid-contact reference electrodes were successfully developed and applied for trace analysis of lead in environmental samples [159-162].

6. Requirements for sensors and measurements in environmental samples

Measurements in environmental samples require reliable sensors, specific conditions of the determination, and relatively inexpensive technology to be implemented (on-site) worldwide. Nowadays, mostly laboratory-based analysis is applied for the determination of water components. Subsequently, a time delay between the sampling and the analysis is inevitable, so the analysis does not always reflect the actual distribution of pollutants [163]. Real-time monitoring is an answer that may be achieved by implementation of sensors in remote places, for example, lakes and rivers. Ideally, an environmental sensor should be characterized by satisfactory performance (resistant to chemo- and bio-fouling), prolonged lifetime (years), be preferably maintenance limited/free (to reduce the costs of servicing), low-powered (equipped with long lasting batteries) or self-powered, for example by microbial fuel cell, and finally coupled into a wireless sensor network with the ability to transfer data over significant distances to the central unit for further processing of the signal [164-168]. Apart from environmental applications, sensors with similar properties may be applied in-vivo and/or in-real time in the entirely different area of bio-tracing of ion concentration in the clinical analysis of body fluids, for example, blood and sweat [169, 170]. Although physical sensors are somewhere close to the proposed (desired) sensor architecture/utility, chemical sensors due to the need of recalibration, bio fouling, and the reliability of analytical methods over time have been intensively investigated, but not yet employed on an industrial scale [171, 172].

Ion-selective electrodes are constantly investigated as an alternative for rather expensive laboratory based instrumentation as well as for use as online sensors for the monitoring of the distribution of pollutants. This is possible by extending the analytical range of ISEs as a result of lowering the detection limit. However the modification of the design of the electrodes and the protocol of the measurement must be as simple as possible because of the restricted operational costs (the measurement protocol and the maintenance of the system). The primary requirement of measurements at low activities in environmental samples is the sufficiently high selectivity of ISEs. It was previously stated that selectivity of ISEs is primarily dictating the low detection limit of plastic membrane electrodes; in fact the *LDL* is determined concurrently by the selectivity and the transmembrane ion fluxes. Although the transmembrane ion fluxes may hinder the response at low analyte activities, they might be optimized to lower the detection limit of ISEs (by optimization of the inner reference solution) [173-175]. This is limited, however, in the analytical applications, as the presence of inner reference solution causes the problem of refilling the inner reservoir of the electrode, of limiting the orientation of the electrode, restrictions to the temperature and the pressure at the measurement point [175].

Another aspect of measurements of environmental samples is the need for recalibration. Depending on the electrode system, at least one point calibration must be performed in a reasonable period of time and/or per number of measurements. The need for recalibration comes from the continuously changing surface (bio-fouling) of the electrode, due to bioactive organisms/substances in the environmental conditions [1]. A partial solution to these problems may be provided by the application of short time measurements or by introducing disposable electrodes with a sufficiently repeatable response [162]. On the other hand, the equilibration process may last for hours until a stable potential is achieved. Thus, the time of the measurement should not exclude the ISE from practical applications if the intention is to measure low concentrations [78, 96, 99, 100]. Additionally, the ionic strength at which calibration and the actual determination are performed should not influence the response of ISEs, so in most cases the calibration is performed at similar ionic strength (by applying appropriate activity of the background electrolyte) to the one estimated in the environmental sample.

In the case of many ions and especially for Pb^{2+} detection, pH during the calibration and the actual measurement is crucial [13]. As the speciation of lead is strongly dependent on changes in pH, lead undergoes hydrolysis in water solutions to a range of hydroxyl complexes. Up to seven hydroxyl complexes have been recognized and described [177]. To obtain total free lead activity, a pH about 4 is usually applied. This is possible however only for laboratory based measurements, while for on-line measurements usually no adjustments to pH are performed (if it is within acceptable pH range) [173].

Finally, from the financial perspective of mass production ISEs for on-line environmental analysis should be as inexpensive as possible, so the design of the electrode and the protocol of the measurement should be uncomplicated. Solution handling, reagents, and waste storage are of significant concern in the environmental system. Those parameters influence the complexity of the sensor device (pumps, valves, and storage), size, and requirements for the maintenance, affecting per-sample and per-measurement costs. Although on-line analysis of pollutants by ISEs is still the holy grail of potentiometry, the determination of pollutants in real environmental samples may yet be very successful [76, 178, 179].

7. Characterization methods

7.1 Potentiometric methods

7.1.1 Zero current potentiometry

Potentiometry has been applied in all scientific publications (***Papers I-VI***) used in this doctoral thesis. The typical potentiometric measurement is performed in two electrode system: the indicator electrode (ion-selective electrode) and the reference electrode. The detailed description of the method was explained in section 2 of this thesis. However it is worth mentioning the fact that potentiometric ion-selective electrodes are among the oldest chemical sensors with origins dating back before the twentieth century. Ion-selective electrodes are especially appreciated in measurements of electrolytes in blood, sweat, and urine. Such ions as K^+, Na^+, Ca^{2+}, Mg^{2+}, H^+, Cl^- may be rapidly measured by ISEs in hospitals around the world allowing fast medical diagnostics [11].

Ion-selective electrodes are sensitive to activity and not to the concentration of ions in the solution. Ionic interactions are the prime cause of the difference between the concentration and the activity. The relation between those two may be expressed by, eq. 17:

$$a_\mathrm{i} = f_\mathrm{i} c_\mathrm{i} \qquad (17)$$

where, a_i is the activity, f_i is the activity coefficient, and c_i is the concentration of i-th ion

The activity coefficient depends on the type of ions present in the solution and the total ionic strength of the solution. The activity coefficient may be estimated using Debye-Hückel theory, eq. 18:

$$\log f_\pm = -\frac{A z_+ z_- \sqrt{I}}{1 + B d_\pm \sqrt{I}} + CI \qquad (18)$$

where, A and B are conditional constants for each sample solution and depending on parameters like temperature, electric permittivity of the solvents, density, z_+ and z_- are the charge numbers for respective cation and anion, I is the ionic strength, $d_\pm$ is the average of effective ion radius (at 25 °C, $d_{Pb^{2+}} \approx 4.5$Å), and C is a experimentally found coefficient approximated to $C = -0.1 z_+ z_-$, for ionic strength up to 0.3 mol dm^{-3} [22, 180].

The ionic strength of the solution is defined by, eq. 19:

$$I = \frac{1}{2} \sum_\mathrm{i} c_\mathrm{i} z_\mathrm{i}^2 \qquad (19)$$

where, c_i is the concentration and z_i is the charge of the i-th ion.

In most of determinations reporting concentration instead of activity is preferred. Consequently, preparation of the empirical calibration curve based on concentration standards (with similar ionic strength to the one in the sample) is performed. When measuring in any sample, one must be sure that the sample is in the range covered by the standards. Additionally, in some cases a total ionic strength adjustment buffer may be added to both the calibration and the sample solutions [11].

Except for the main parameters of formal potential, sensitivity and the selectivity, ISEs may be described by other parameters, which are: potential stability, response and recovery time, reproducibility of measurements, pH and redox sensitivity and the lifetime. The response of the ion-selective electrode is stable enough if the measured signal is not drifting or varying in random matter. However, drift of potential may occur owing to the unstable potential of the reference electrode or changes in the formal potential of the ISEs. Furthermore, the time which passes from the first contact of the electrode system with the measuring solution until stabilisation of the potential (steady-state) is called the response time. The steady-state is usually achieved within minutes; but a requirement for some measurements leads to analysis being performed under non-equilibrium conditions, for example in clinical analysis. The recovery time is the time that elapses before the electrode is ready to be used for measurement in another sample. For industrial applications a number of samples per certain period of time may be estimated by introducing response and the recovery time. Another factor is reproducibility, which determines what the accuracy of potentiometric measurements is within electrodes prepared in the same manner. Furthermore, the influence of pH and redox active species on the performance of ISEs is a matter of concern. Finally, the lifetime of the electrodes may be defined as storage (shelf) and operational (use) lifetime, and optimal conditions for storage and measurements. The operational lifetime of electrodes may vary from single use (disposable ion-selective electrodes) to months, and even years [181, 182].

7.1.2 Non-zero current potentiometry (chronopotentiometry)

The Chronopotentiometric measurements were performed using a three electrode system, for example with a working, a reference, and a counter electrode. For this, the constant currents were applied to the ISE (working) electrode. When the applied current was passed through the working and the counter electrodes, the ISE was polarized and its potential changed. At the same time the potential is measured as a function of time, between the working and the reference electrodes [191].

In ***Papers V and VI*** chronopotentiometry was used to study the behaviour of solid-state PbS/Ag_2S membrane electrodes under the conditions of constant current (polarization) applications in the development of the novel method for the determination of ionized lead in environmental samples.

7.2 Voltammetric methods

7.2.1 Cyclic voltammetry (CV)

In voltammetric methods the current at the working (polarized) electrode is sampled as a function of potential applied to the electrode. Among all voltammetric methods cyclic voltammery is the most frequently used to obtain qualitative information about electrochemical reactions at the electrode surface, for example thermodynamics of redox processes, kinetics of heterogeneous electron transfer reactions, and coupled reactions or adsorption processes. Measurements are usually performed in unstirred solutions. By cycling the potential of the working electrode, current obtained at the working electrode is constantly measured. The potential range and the scan rate (mV s^{-1}) may be adapted to the conditions required for the investigated species and/or process. According to the needs, the potential cycles can be repeated continuously. In particular, the possibility of repetitive cyclic polymerizations can be beneficial for the electrosynthesis of conducting polymers on electrode surfaces. By applying cyclic voltammetry it is possible to follow from cycle to cycle the continuous growth of the electroactive material at the surface of a working electrode. Measurements are performed in the three electrode system consisting of working electrode (electrochemically inert over a wide range of potential window, for example glassy carbon, gold, platinum), reference electrode (usually quasi reference electrode consisting of Ag wire coated with AgCl or commercially available conventional Ag | AgCl | 3 mol dm^{-3} KCl reference electrode) and counter electrode, for example Pt wire (to support the generated current, the surface of the counter electrode should be equal or larger than the one of working electrode) [11, 183, 184].

Cyclic voltammetry was used to electrosynthesize polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(benzopyrene) (PBP) films on glassy carbon disk electrodes from their respective monomers by cycling the potential in the presence of eriochrome black T (EbT). Obtained films were further applied either as Pb^{2+} selective membranes (***Paper II***) or as an ion-to-electron transducer in solid-contact Pb^{2+}-ISEs (***Paper III***).

7.2.2 Differential pulse anodic stripping voltammetry (DPASV)

The DPASV is a method where the current is measured as a function of the time after applying a potential step (pulse). The pulse voltammetry was developed to lower the detection limit of voltammetric measurement by suppressing the charging background current. Among pulse voltammetric measurements, one of the methods for improving the faradaic to charging current ratio is differential pulse voltammetry. In this method fixed magnitude pulses (superimposed on a linear potential ramp) are applied to the working electrode just before the end of the drop. To enhance the sensitivity of the measurement the current is sampled twice, just before the application of the pulse and again later in the lifetime of the pulse when the charging current decays. The difference of the second and first current is then plotted against applied potential. The resulting voltammograms consist of current peaks with the height being directly proportional to the concentration of the investigated species. This method may be successfully implemented in the stripping mode which allows simultaneous determination of various species in the nanomolar concentration range. Stripping analysis is realized in two steps. Firstly, a deposition step when a fraction of the metal ions is deposited on the surface of the working electrode (also called pre-concentration step). Secondly, a stripping step is performed when dissolution of the previously obtained deposition is applied [11, 183].

In ***Paper VI*** differential pulse anodic stripping voltammetry was applied to determine the concentration of lead in the environmental sample.

7.3 Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry is a technique in which total concentration of various species can be determined. The technique consists of inductively coupled plasma (ICP) coupled with mass spectrometery (MS). ICP operates at atmospheric pressure and high temperatures while MS requires vacuum pressure and low temperatures, so the instrumentation use for ICP-MS is very complex. The technique is mainly used for liquid samples; however in laser ablation mode solid samples may be investigated. Firstly, the sample is nebulised into the plasma and part of the spray is taken by the stream of argon and further undergoes volatilisation, atomisation, and finally ionisation. Subsequently, the sample reaches the detector (mass analyzer which is usually based on an electron multiplier) where the signal is received and amplified. With a highly sensitive detector the determination may be performed from complex matrix at ultra trace concentration level, simultaneously for multiple species. The content of the sample is determined by the specific mass-to-charge ratio for various ions obtained in the ionisation process. The quantitative analysis of the sample is performed by prior calibration with elemental standards [188, 189].

In ***Papers III, IV, V, and VI*** inductively coupled plasma mass spectrometry was used as a reference method for potentiometry to determine lead concentrations in various samples.

7.4 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy is a technique used to characterize the electrical properties of materials and interfaces. In studies of the properties of potentiometric ion sensors it is used to describe ion transport and electronic properties of conducting polymer films and ion-selective membranes. The EIS measurement is realized in a three electrode system consisting of working, reference and counter electrodes. The electrodes stay at open circuit potential until an alternating small amplitude sinusoidal excitation signal is applied to perturb the cell. The measurement is performed at various frequencies (usually between 1 mHz and 1 MHz) resulting in the current where, its phase angle with respect to applied perturbation at its frequency is measured. The amplitude of the excitation signal must be sufficiently small in order to obtain linear response. From data an equivalent electrical circuit model can be obtained to extract valuable information on the electrochemical system. The impedance (*Z*) represents a complex quantity given by the eq. 20:

$$Z = \frac{E'}{I'} \mathrm{e}^{-\mathrm{j}\phi} \tag{20}$$

where j is imaginary number, $\mathrm{j} = \sqrt{-1}$; and ϕ is a phase angle between sinusoidal voltage (E') and current (I') [185, 186, 187].

In ***Paper I*** electrochemical impedance spectroscopy was used to study differences between the poly(vinyl chloride) and polyacrylates based membranes in conventional $\mathrm{Pb^{2+}}$-selective electrodes.

7.5 Differential scanning calorimetry (DSC)

Differential scanning calorimetry is a thermoanalytical technique. The measurement is realized in the same mode for the sample and the reference, where the temperature of both is increasing linearly in time. As a result, the difference in the amount of heat to increase the temperature of a sample and the reference is measured as a function of the temperature. DSC is use to measure the amount of heat absorbed or released during the phase transition of the sample by observing the heat flow between the sample and the reference material [192].

In ***Paper I*** the DSC was used to investigate glass transition temperatures of isododecyl acrylate (IDA), acrylonitrile (ACN) and 1,6-hexanediol diacrylate (HDDA) co-polymers.

7.6 Field emission gun scanning electron microscopy (FEG-SEM)

Scanning electron microscopy is a technique used for imaging the investigated surfaces. In electron microscopy where the wavelength of electrons is much smaller than the wavelength of the visible light, the diffraction effects occur at much smaller physical dimensions resulting in greater resolution than in light microscopy. Furthermore, a field emission gun which is used to produce an electron beam that probes the surface is much smaller in diameter, with much greater current densities or brightness, and more coherence than thermionic emitters. However there is a limitation only to non-living objects, since during the measurement a vacuum is required as well as a preparation of the samples, freezing, fixation or dehydratation, for example, must be applied. The main principle of scanning electron microscopy is based on probing the surface with primary electrons resulting in images from secondary electrons that are emitted from the surface due to the excitation by the primary electron beam. SEM is used to investigate surface morphology (shape, size, and the arrangement of particles), topography (the surface features of an object and their texture), and composition (if the elements and compounds of the sample and their relative rations may be investigated, for example by energy-dispersive X-ray) [189, 190].

In ***Paper II*** field emission gun scanning electron microscopy was used to study the morphology of electosynthetiszed polybenzopyrene films doped with eriochrome black T before and after conditioning in lead(II) nitrate solutions.

7.7 Energy Dispersive X-ray Spectrometry (EDAX)

Energy dispersive X-ray spectrometry is an analytical technique used for elemental analysis. In particular when the incident electron beam hits the surface of the sample, electrons from the inner shell of atoms are excited and ejected, creating an electron hole. Subsequently, the electron from outer shell (higher energy shell) fills the hole and the difference in energy between the outer and inner shells is released in the form of X-ray radiation. Emitted X-ray energy is then measured by an energy dispersive spectrometer.

Since the energy of X-ray radiation of the difference in energy between the two shells and of the atomic structure for each element are characteristic for every element, qualitative analysis may be performed [191, 192].

In ***Paper II*** energy dispersive X-ray spectrometry was used to investigate the presence of lead in unconditioned and conditioned polybenzopyrene doped with eriochriome black T films.

8. Results and discussion

8.1 Conventional Pb^{2+}-ISEs based on polyacrylate membranes

The work focussed on the goal to achieve lower detection limits of Pb^{2+}-ISEs was started with polymeric membranes, which were conventional type polyacrylate-based electrodes in order to diminish the transmamberne ion flux of primary ion from the reference to sample solution (***Paper I***). Subsequently, the polyacrylate membrane was based on isododecyl acrylate (IDA), acrylonitrile (ACN) and 1,6-hexanediol diacrylate (HDDA) co-monomers. Previously, the same material was used for preparation of planar electrodes [193-195]. However, initiation of the polymerization was obtained by UV light irradiation which may interact with the membrane components and affect their properties, leading to their decomposition or inhibition of the polymerization process. Therefore thermo-polymerizable membranes were introduced for the preparation of the Pb^{2+}-ISEs.

Table 1. Glass transition temperature and mass loss of prepared IDA/ACN/HDDA polymers.

Amount of AIBN [wt.%]	Heating time [h]	Heating temperature [ºC]	Glass transition temperature T_g [ºC]	Weight loss [%]
0.5	1	60	–115. 9	41.98
		70	–111.9	14.48
	2	60	–98.5	2.21
		70	–80.7	1.63
	3	60	–85.2	2.49
		70	–65.5	0.13
1	1	60	–85.7	5.54
		70	–74.7	0.12
	2	60	–63.6	0.18
		70	–71.6	0.69
	3	60	–58.9	0.20
		70	–67.5	2.25
3	1	60	–68.1	1.83
		70	–69.2	0.72
	2	60	–64.3	1.73
		70	–67.8	2.05
	3	60	–59.3	2.54
		70	–65.9	2.09

To find the best conditions for thermopolymerization of IDA/ACN/HDDA mixture the influence of thermoinitiator content as well as the time and temperature of the heating process were investigated. Polymerization carried out at 50 °C led to polymers of a liquid consistency, whereas polymers obtained at 80 °C were hard and brittle. For this reason, only polymers obtained by heating in 60 and 70 °C were further tested. The obtained polymers were thermally analyzed using DSC. The results of the experiment are presented in Table 1.

The lowest values (below –110 °C) of glass transition temperature (T_g) were obtained for polymers containing 0.5 wt.% of the initiator which were heated for only 1 h at both 60 and 70 °C. The T_g values increased together with the initiator content and heating temperature. To ensure stable working parameters for the ion-selective electrodes based on polyacrylate membranes, any leaching of the polymerization products must be avoided. Therefore the obtained samples were subjected to extraction in a Soxhlet apparatus with distilled water. Extraction was carried out for 24 h for every sample. The results of the test are presented in Table 1. A significant weight loss (up to 40 wt.%) was found for the samples of the lowest T_g. This result may indicate that those samples were not fully polymerized. The lowest leaching (less than 0.2 wt.%) was observed for polymers containing 1 wt.% of AIBN heated for 2 or 3 h at 60 °C, or for 1 h at 70 °C as well as for the polymer containing 0.5 wt.% of AIBN heated for 3 h at 70 °C. Considering both the mass loss and the glass transition temperature, the polymer containing 1 wt.% of AIBN and heated for 1 h at 70 °C was considered the best for ISE preparation.

Studies on Pb^{2+}-ISEs have been carried out using commercially available lead(II) ionophores. Preliminary examinations showed that incorporation of lead ionophore II (S,S′-Methylenebis(N,N-diisobutyldithiocarbamate)) or III (N,N,N′N′-Tetradodecyl-3,6-dioxaoctanedithioamide) causes inhibition of the polymerization process. Lead ionophore IV (tert-Butylcalix[4]arene-tetrakis(N,N-dimethylthioacetamide)) appeared to be insoluble in a mixture of membrane co-monomers. Thus, uranyl ionophore I (N,N′-Diheptyl-N,N′,6,6-tetramethyl-4,8-dioxaundecanediamide), reported earlier as a good lead ionophore in PVC-based membrane [196], was successfully applied in this work. For comparison, a PVC-based membrane was prepared with the same ionophore. The potentiometric sensitivity to Pb^{2+} for PVC-, polyacrylate-based, and a solid-state (PbS/Ag_2S) membrane ISEs are shown in Figure 4 A. The slope of the linear part of the calibration curves for all types of electrodes (10^{-2}-10^{-5} mol dm^{-3} $Pb(NO_3)_2$) was close to Nernstian (solid-state membrane, s= 25.0 mV dec^{-1}; PVC-based membrane, s= 29.2 mV dec^{-1}; and polyacrylate-based membrane, s= 28.0 mV dec^{-1}). The detection limit for all three types of ISEs (under the same conditions) was similar and close to 10^{-6} mol dm^{-3}.

The possibilities of lowering the detection limit of the polyacrylate electrode are shown in Figure 4 B. The electrodes with an internal reference solution containing 8×10^{-11} mol dm^{-3} Pb^{2+} were used to inspect the ISEs responses below the micromolar concentration range. The PVC-based electrode showed a super-Nernstian response (indication of transmembrane ion fluxes), while the response of both polyacrylate-based and solid-state Pb^{2+} ISE was unaffected by the internal solution change and similar to that in Figure 4 A.

This response may be attributed to the lower diffusion coefficient of Pb^{2+} in the polyacrylate matrix in comparison with the PVC membrane.

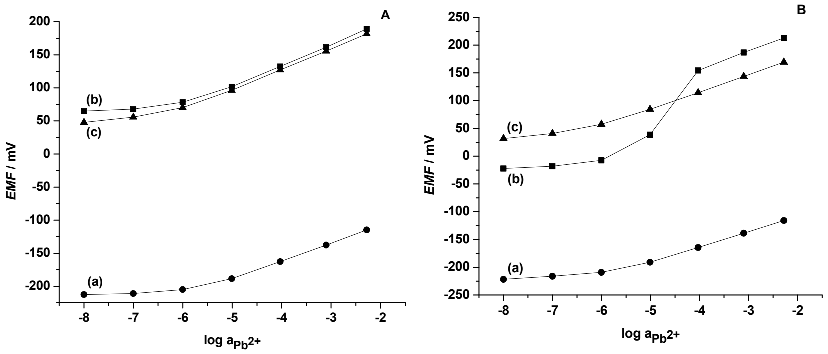

Figure 4. Response of Pb^{2+}-ISEs: (a) solid-state PbS/Ag_2S electrode, (b) PVC-based electrode, (c) polyacrylate-based electrode with A) the internal solution for (b) and (c) electrodes contained 10^{-3} mol dm^{-3} $PbCl_2$, and B) the internal solution for the (b) and (c) electrodes contained 10^{-3} mol dm^{-3} $PbCl_2$, 10^{-2} mol dm^{-3} Na_2EDTA (calculated $a_{Pb^{2+}} = 8\times10^{-11}$ mol dm^{-3} for pH= 3.6), 10^{-2} mol dm^{-3} NaCl.

Electrochemical impedance spectroscopy (EIS) was applied in order to inspect the differences between the membranes with various matrices. Previously it was reported that the ion-transport of the methacrylic-acrylic-based electrodes is much slower than in the PVC-based electrodes. The apparent diffusion coefficients for lead ion in methacrylic-acrylic-based electrodes was of the order 10^{-12} to 10^{-11} cm^2 s^{-1} while for the PVC-based electrode approximately a thousand times higher value was reported [41]. The same behaviour could be expected for the polyacrylate electrodes in comparison with the PVC based electrodes. The impedance spectra of PVC-based and polyacrylate-based electrodes are shown in Figure 5.

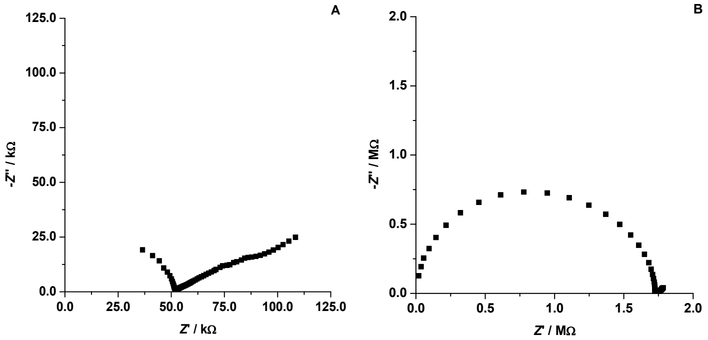

Figure 5. Impedance spectra of: A) PVC-based electrode and B) polyacrylate-based electrode.

The high frequency semicircles show that the bulk resistance was approximately 50 kΩ for the PVC-based electrode and about 1.7 MΩ for the polyacrylate-based electrode. The geometric (bulk) capacitance was about 18 pF for the PVC-based electrode and about 11 pF for the polyacrylate-based electrode, which indicates that the polyacrylate-based membrane has a lower dielectric constant than the PVC-based membrane (assuming that the film thickness and area are the same for both membranes). Both electrodes exhibited a linear branch in the low frequency part of the spectra. However the slope was significantly less than 0.5 and thus showed some deviation from a classical Warburg diffusion process. None the less, 35 times smaller bulk resistance registered for the PVC-based electrode than the polyacrylate-based electrode indicated decreased ions diffusion rates inside the polyacrylate in comparison with the PVC membrane. The low diffusion rate of Pb^{2+} ions in the polyacrylate membranes makes them good candidates for lowering the detection limit of lead ion-selective electrodes. This membrane material however, could be directly applied in conventional type of Pb^{2+}-ISEs to stop transmembrane ion fluxes. Since the direction of the further research of lowering the detection limit of Pb^{2+}-ISEs focused exclusively on all-solid-state membranes the idea of applying polyactrylate membranes was not pursued further at this point.

8.2 Development of the solid-contact material for Pb^{2+}-ISEs

Undesired properties of conventional type of Pb^{2+}-ISEs provoked by the internal filling solution initiated my research on the application of solid-contact electrodes for determining Pb^{2+}. Poly(3,4-ethylenedioxythiophene) (PDOT), polypyrrole (PPy), and polybenzopyrene (PBP) doped with eriochrome black T (EbT) were investigated as solid-contact for Pb^{2+}-sensitive electrodes (***Paper II***).

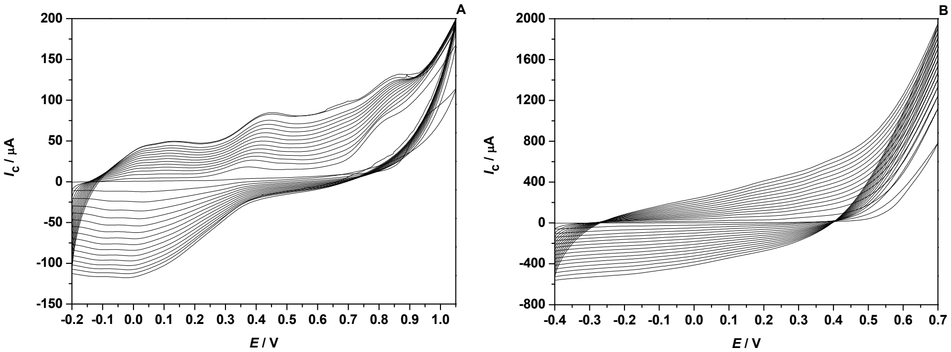

Figure 6. Electrosynthesis of A) PEDOT and B) PPy in EbT water solution (scan rate: 50 mV s^{-1}, 15 scans).

Polymeric films were electrosynthesized on glassy carbon disk electrodes from their respective monomer by cyclic voltammetry in the presence of eriochrome black T. Cyclic voltammograms recorded during electrosynthesis of PEDOT and PPy in EbT/water solution are presented in Figures 6 A and B, respectively. Cyclic voltammetry was a method of choice for electrosynthesis of polymeric films, as it gives a unique possibility for an inspection of the polymer growth with each potential cycle, in comparison with galvanostatic or potentiostatic processes. In the case of PEDOT(EbT), two well resolved oxidation peaks were observed at ca. 0.4 and 0.8 V. During reduction, a broad peak can be observed around 0 V. For both PEDOT and PPy cases polymer growth was continuous. In contrast, during synthesis of PPy no redox peaks could be distinguished. Electrosynthesis of PBP in the presence of EbT is shown in Figure 7 A.

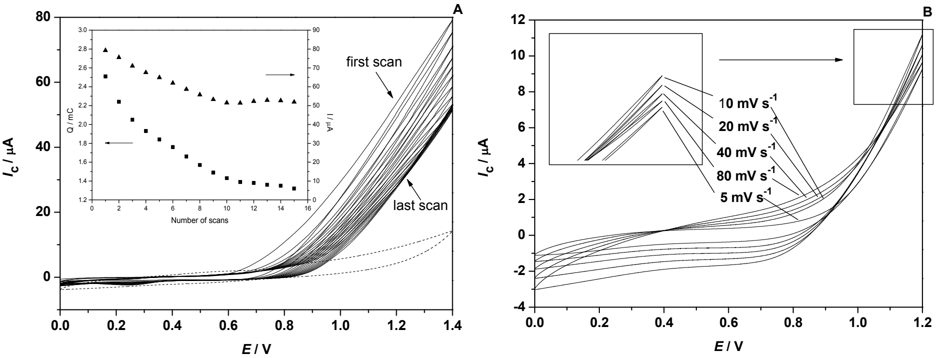

Figure 7. A) Electrosynthesis of PBP(EbT) in EbT-ACN solution (scan rate: 20 mV s^{-1}, 15 scans). Note: with dashed line the background current is marked. Insert: the compiled graph of total charge values and maximum current during potential scanning. B) Potential scanning of the PBP(EbT) film at various scan rates to 1.2 V in EbT-ACN monomer free solution (scan rate: 20 mV s^{-1}, 3rd scan).

The subsequent potential scanning results in continuing film growth to approximately 0.37 µm thickness of PBP(EbT). This thickness value is, however, a rough estimation from total charge which passed during synthesis. The beginning of PBP synthesis is probably connected with an oxidation/reduction of EbT at the electrode surface and oxidation (formation) of partly soluble BP units. Consequently, the PBP film was growing since, with each scan, film resistance is increasing and both the maximum current and total charge are decreasing linearly. The deposition process is still affected by oxidation and reduction of EbT, but this process occurs now on already formed PBP film. After the 10th scan the PBP stops growing and the electrochemical response is mainly due to oxidation/reduction of the film. The p-doping at various scan rates of PBP is presented in Figure 7 B. The main source of the capacitive current is due to the working electrode. At 0.8 V the current is increasing due to oxidation/reduction of PBP film. The maximum current is ca. 10 μA. Furthermore, the electrochemical response of the PBP(EbT) film during doping is independent of the scan rate. Since the charge values are slightly decreasing with an increasing scan rate, the electron transfer is not diffusion limited. This could be explained by relatively small film thickness as well as by the structure of PBP(EbT) film. EbT anion acts as a counter ion and its diffusion is limited due to a relatively large size. The ionic conductivity of used EbT/ACN solution is ca. 100 times lower than the ionic conductivity of 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate/ acetonitrile solution (TBAPF$_6$/ACN). In comparison, ionic conductivity of 50 mmol dm^{-3} EbT/water solution is about 10% of 0.1 mol dm^{-3} KCl. Hence electrosynthesized PBP films are thinner when compared with films polymerized from EDOT and Py with EbT. On the other hand, PBP have strong adhesion to the glassy carbon surface, making the PBP based electrode a good candidate to serve as a simple and robust contact material/chemical sensor.

Eriochrome black T has strong affiliation to Pb^{2+} as defined by a high stability constant of complexation ($\log K_{\mathrm{PbL}}^{\mathrm{PbL}} = 13.19$ [197]). Subsequently, field emission gun scanning electron microscopy (FEG-SEM) was applied to investigate the surface PBP(EbT) films before and after conditioning in 0.1 mol dm^{-3} Pb(NO$_3$)$_2$ solution. The results are presented in Figure 8.

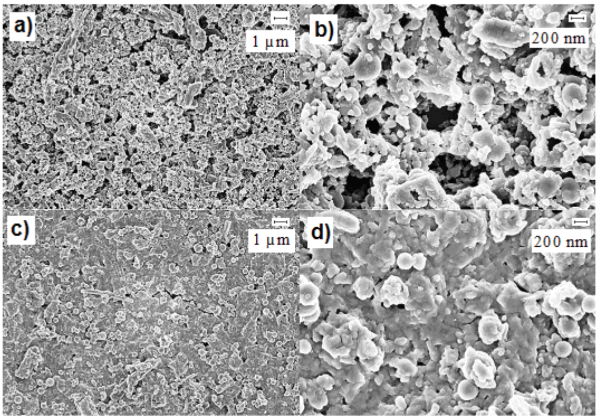

Figure 8. FEG-SEM images of unconditioned PBP films (a, b) and conditioned films in 0.1 mol dm^{-3} Pb(NO$_3$)$_2$ (c, d) with 5000 and 25000 magnifications.

Conditioned films were in contact with conditioning solution for two days before the measurements. All films exhibit uniform coverage on the glassy carbon surface with a “cauliflower like” and highly porous structure.

Due to the complexation properties of eriochrome black T, all obtained solid-contact materials were further used to investigate their potentiometric response to Pb^{2+} (***Paper II***).

The ion-selective electrodes were based on conducting polymer used as a sensing membrane. In this case the conducting polymer acted as an ion-to-electron transducer and was also responsible for the sensitivity toward Pb^{2+}, eliminating the need for previously applied inner reference solution in the conventional type of Pb^{2+}-ISEs.

8.3 Pb^{2+}-ISEs based on various conducting polymers doped with eriochrome black T

Ultimately depending on the eriochrome black T complexation abilities toward Pb^{2+}, the sensitivity toward Pb^{2+} was induced by conditioning PEDOT, PPy, and PBP doped with EbT films in 0.1 mol dm^{-3} $Pb(NO_3)_2$ solution (***Paper II***). The potentiometric sensitivity to Pb^{2+} for various conditioning times is shown in Figure 9. For all potentiometric measurements the solid-state PbS/Ag_2S membrane lead-selective electrode was applied to monitor changes in the activity of ionized lead (the trend was marked by the dashed line in Figure 9).

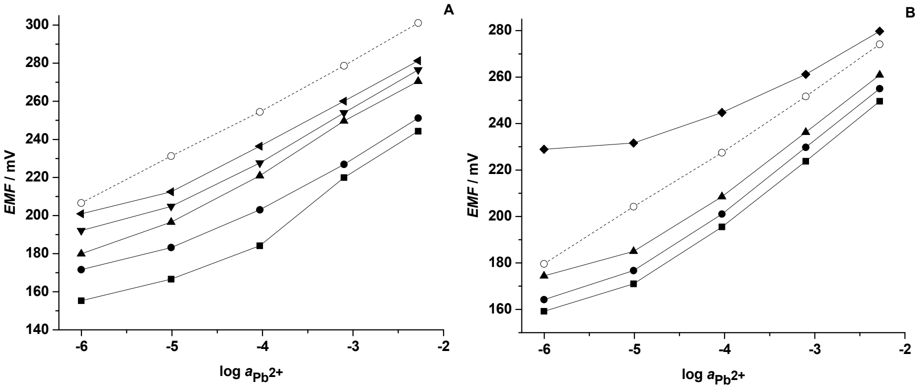

Figure 9. Calibration in lead $Pb(NO_3)_2$ for various conditioning times: A) PEDOT(EbT) electrode ■ 1day, ● 2days, ▲ 4 days, ▼ 6 days, ◀ 9 days, B) PPy(EbT) electrode after ♦ 2 weeks, and PBP(EbT) electrode ■ 1day, ● 2days, ▲ 7 days. In both cases: ○ solid-state PbS/Ag_2S electrode.

After one day of conditioning the PEDOT(EbT) electrode exhibited super Nernstian response between 10^{-3} and 10^{-4} mol dm^{-3} $Pb(NO_3)_2$. However, this effect was replaced with close to Nernstian response already after two days of conditioning with slopes: 2 days (24.9 mV dec^{-1}), 4 days (27.1 mV dec^{-1}), 6 days (26.3 mV dec^{-1}), and 9 days (25.2 mV dec^{-1}). PPy(EbT) electrode exhibited sub-Nernstian response with slope of calibration curve 17.6 mV dec^{-1} after 2 weeks of conditioning. No improvement was registered for longer conditioning time. For the PBP(EbT) electrode, the slope already after one day of conditioning was close to Nernstian: 1 day (28.8 mV dec^{-1}), 2 days (28.7 mV dec^{-1}), and 7 days (27.8 mV dec^{-1}). Finally, the solid-state PbS/Ag_2S membrane electrode slope was 25.6 mV dec^{-1}. For all applied electrodes a similar low detection limit was obtained, close to 10^{-5} mol dm^{-3} Pb^{2+}.

The difference between each investigated solid-contact material was observed when checking the so called “memory effect” for each film. The hysteresis of PEDOT, PPy, and PBP doped with EbT electrodes is shown in Figure 10.

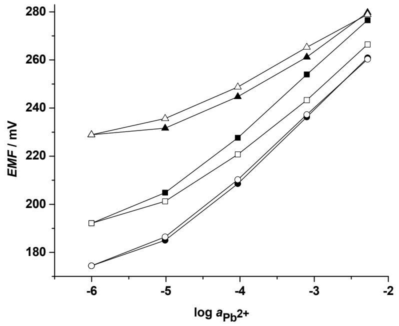

Figure 10. Hysteresis of Pb^{2+}-sensitive films: ▲ PPy(EbT), ■ PEDOT(EbT), ● PBP(EbT), where filled symbols refer to the calibration done from higher to lower activity of primary ion, while unfilled symbols refer to the calibration done from lower to higher activity of primary ion.

The hysteresis was determined by the difference in potential at a certain Pb^{2+} activity between calibration performed from higher to lower and from lower to higher activity of Pb^{2+}. PPy(EbT) films suffered from low sensitivity with an average hysteresis of about 5 mV. The PEDOT(EbT) film showed significant hysteresis of about 11 mV at higher range of lead activity. On the other hand, the hysteresis was much smaller for the PBP(EbT) electrode with an average value of 1 mV along the entire calibration curve. Similar behaviour was observed for solid-state PbS/Ag_2S for which it was 0.6 mV.

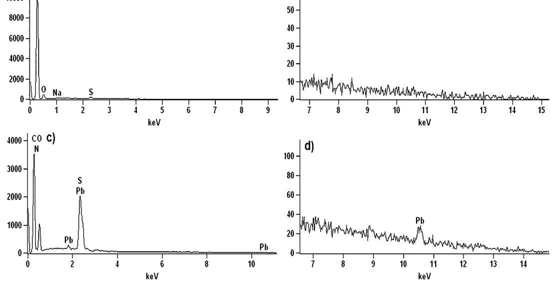

Figure 11. EDAX elemental analysis of PBP films, where: a, b are results from unconditioned films and c, d represents conditioned films in 0.1 mol dm^{-3} $Pb(NO_3)_2$.

PBP(EbT) films did not exhibit any memory effect and were further investigated in aspects of Pb^{2+} interactions with the membrane. Polymeric films were subjected to elemental analysis (EDAX) before and after conditioning in 0.1 mol dm^{-3} $Pb(NO_3)_2$ solution. Results were gathered in Figure 11. The unconditioned films did not produce any signal from lead. On the contrary, conditioned films produced a signal from lead inside the structure of PBP films. Signals from lead were observed at approximately 2.4 keV and 10.6 keV. Evidence of lead inside the investigated films indicates that, as expected, during the conditioning lead is inserted into PBP films.

To conclude, electrosynthesis of PBP with immobilization of eriochrome black T as a dopant was achieved. The formation of thin films occurred. The thickness of the film appears to be advantageous for fast and stable response of the electrode. PBP(EbT) films exhibit high stability of the potential readouts, sufficient reproducibility of the calibration curves and minor hysteresis. Moreover, the investigation indicates that PBP is significantly better as a platform for lead sensing than PPy and PEDOT used in the same arrangement. Since the selectivity of obtained PBP (EbT) films ultimately is dependent on complex strength, no direct lowering of the detection limit was possible. For instance, this indicator binds to a similar or even to better extent other divalent ions described by the following association constants: cadmium ($\log K_{\mathrm{CdL}}^{\mathrm{Cd,L}} = 12.74$), cobalt ($\log K_{\mathrm{CoL}}^{\mathrm{Co,L}} = 20.0$), magnesium ($\log K_{\mathrm{MgL}}^{\mathrm{Mg,L}} = 20.0$), or zinc ($\log K_{\mathrm{ZnL}}^{\mathrm{Zn,L}} = 12.9, \log K_{\mathrm{ZnL_2}}^{\mathrm{Zn,L}} = 20.0$) [198]. However, owning to the potential stability (lack of hysteresis) and the additional driving force to take up Pb^{2+} from the sample solution, PBP films make a good candidate as an ion-to-electron transducer layer in solid-contact Pb^{2+}-ISEs for lowering the detection limit.

8.4 Lowering of the detection limit of solid-contact Pb^{2+}-ISEs

Solid-contact Pb^{2+}-selective electrodes (Pb^{2+}-ISEs) were prepared by applying polybenzopyrene doped with eriochrome black T as solid contact material and coating it with conventional poly(vinyl chloride) membrane containing lead ionophore IV (***Paper III***). The method used with the solid-contact Pb^{2+}-ISEs to lower the detection limit was based on concentration and time-dependent conditioning of the electrodes (20 min in 10^{-5} mol dm^{-3} Pb^{2+} for each conditioning cycle). The renewable response was based on partially reversing the flux of primary ions from the membrane to the solution. The response of the solid-contact Pb^{2+}-ISE after each conditioning cycle (7 calibrations in total) is shown in Figure 12 A. Strict protocol of measurement was kept to ensure that the changes of the response are due to the conditioning procedure. To illustrate the changes in the response of ISEs the calibration curves were aligned from the first to seventh conditioning cycle, regardless of the formal potential of ion-selective electrodes. The first calibration curve exhibits super Nernstian response between 10^{-6}-10^{-8} mol dm^{-3} Pb^{2+}. This effect is well known for unconditioned membranes, where the concentration of analyte at the membrane | sample interface is depleted due to faster uptake of ions into the membrane than their transport from the bulk of the solution to the membrane surface [120].

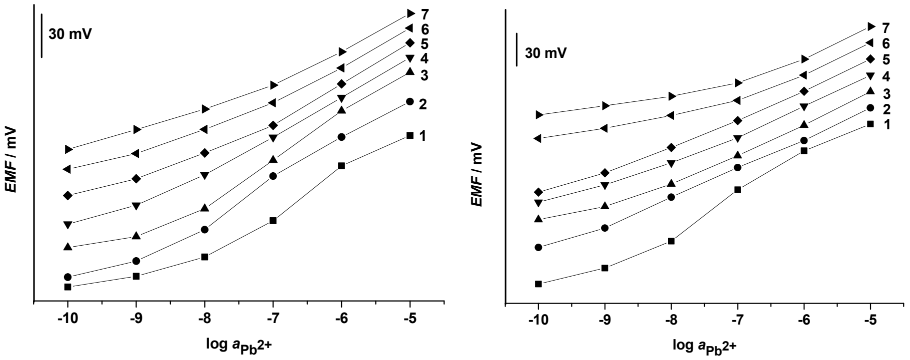

Figure 12. The response of solid-contact lead-selective electrode when applying conditioning cycles (seven conditioning cycles in total, responses aligned and numbered from first to last). Measurements were done in unbuffered solutions (from 10^{-5} to 10^{-10} mol dm^{-3} $Pb(NO_3)_2$: A) first contact with Pb^{2+} solutions, B) after the recovery process was applied.

Gradually, with every next conditioning cycle the super Nernstian response diminished, resulting in Nernstian response after the third conditioning cycle with a slope of 30.9 mV dec^{-1} and detection limit down to pPb^{2+}= 8.7. However the optimal conditioning time to lower the detection limit was established after the fourth cycle (in total 80 minutes conditioning in 10^{-5} mol dm^{-3} Pb^{2+}) with a slope of 26.6 mV dec^{-1} down to pPb^{2+}= 9.3. Further conditioning resulted in increase of detection limit, and finally the *LDL* of Pb^{2+} ISE was established at the approximately constant level reported for electrodes based on lead ionophore IV (~10^{-7} mol dm^{-3} Pb^{2+}) [199]. Loss of sensitivity in the lowest concentration range can be attributed to saturation of the ion-selective membrane (ISM) with Pb^{2+}. When the ISM is in equilibrium with lead ion in the solution, no lowering of the detection limit may be observed. Reaching a lower detection limit is possible only when the concentration of primary ion in the ISM is optimized similarly as in case of conventional solvent polymeric membranes with internal reference solution [121, 123]. However, due to the lack of inner filling solution the optimization of the response is done here by repeating conditioning cycles.

When loss of sensitivity between 10^{-7}-10^{-9} mol dm^{-3} Pb^{2+} occurred, an *LDL* recovery procedure was applied (electrodes were placed for 24 hours in 10^{-3} mol dm^{-3} Na_2EDTA). In Figure 12 B the response of solid-contact Pb^{2+}-ISE is presented after renewing the response by partially reversing the primary ion flux (from the membrane and solid-contact to the recovery solution) and introducing sodium to the membrane. By applying seven conditioning cycles the low detection limit was investigated. After the first conditioning cycle, the electrode exhibits super Nernstian response between 10^{-6}-10^{-8} mol dm^{-3} Pb^{2+}, similar to the case when the membrane did not have any prior contact with primary ion before the measurement. Soaking the electrode in 10^{-3} mol dm^{-3} Na_2EDTA caused partial removal of accumulated lead from the membrane, resulting in renewable response (driven by an ion uptake) in the diluted solutions. By applying a ligand (EDTA) which strongly complexes lead ion (stability constants: $\log K_{\mathrm{PbL}}^{\mathrm{Pb,L}} = 18.0$, $\log K_{\mathrm{PbL_2}}^{\mathrm{Pb,L}} = 2.9$ [198]) and the introduction of Na^+ to the membrane [154] a sufficient decrease of Pb^{2+} was achieved. The EDTA is too large to enter the membrane and any possible surface accumulation of that component was washed off with deionized water after soaking in the recovery solution, thus the responses at nanomolar concentrations are attributed to the partial removal of lead from the membrane/solid-contact layer. The new established state of the membrane allows the detection limit to be lowered to approximately $pPb^{2+} = 9$ already after the second conditioning cycle (retaining up to four conditioning cycles), which indicates that only a small fraction of lead was removed. From the sixth cycle, the *LDL* was established at around 10^{-7} mol dm^{-3} Pb^{2+}. The mechanism behind the recovery of the response is schematically illustrated by the simplified concentration profiles in Figure 13.

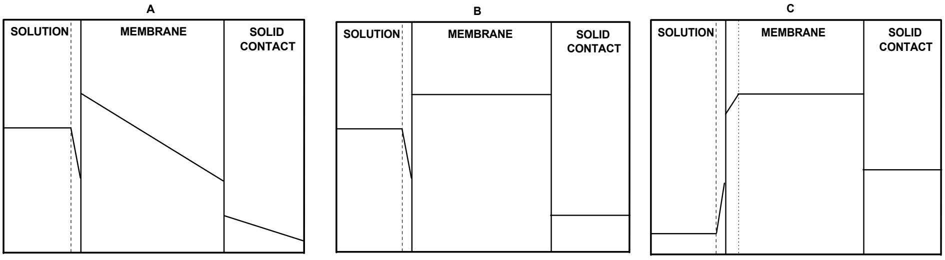

Figure 13. Simplified concentration profiles for solid-contact Pb^{2+}-ISEs for: A) unconditioned membrane, B) well conditioned membrane, and C) when partially reversing primary ion flux by applying recovery process.

When the membrane has not been in contact with primary ion, rapid uptake of Pb^{2+} occurs and the flux of Pb^{2+} is realized from the solution to the membrane. Additionally, a driving force to uptake Pb^{2+} from the solution is realized by the ion-to-electron transducer layer by eriochrome black T in polybenzopyrene film, which has a strong affiliation to ionized lead, $\log K_{\mathrm{PbL}}^{\mathrm{Pb,L}} = 13.19$ [197] (Figure 13 A). Subsequently, when the membrane was saturated with Pb^{2+} the concentration of primary ion inside the membrane was approximately constant. The driving force for lowering the detection limit was then eliminated, thus no significant improvements in the response at low concentrations were obtained (Figure 13 B). The approach to partially reverse the Pb^{2+} flux creates a possibility to renew the response at extremely low concentrations. By applying a strong complexing agent in the solution and introduce Na^+ to the membrane, the flux of ions was reversed, resulting in partial removal of Pb^{2+} from the membrane as well as removal of all ionic impurities and traces of lead by complexation with EDTA (Figure 13 C). The process is effective enough to retain a lower detection limit up to a few measurements.

Up to this point, conditions were simplified to pure, unbuffered solutions. However measurements in environmental samples are performed at higher ionic strength. Consequently, the influence of background electrolyte (10^{-3} mol dm^{-3} KNO_3) was investigated. The results of the conditioning procedure are shown in Figure 14.

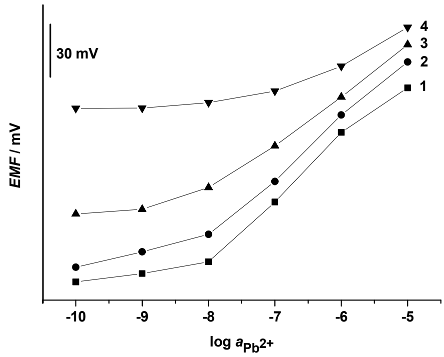

Figure 14. The response of the solid-contact lead-selective electrode when applying each conditioning cycle (four conditioning cycles in total, responses aligned and numbered from first to last). Measurements were done in unbuffered solutions (from 10^{-5} to 10^{-10} mol dm^{-3} $Pb(NO_3)_2$ with constant background electrolyte 10^{-3} mol dm^{-3} KNO_3) after the recovery process was applied.

As previously shown, the first conditioning cycle resulted in super-Nernstian response between 10^{-6}-10^{-8} mol dm^{-3} Pb^{2+}. With the next two conditioning cycles the linearization of the response occurred down to $pPb^{2+}\sim 8$. Further conditioning cycles negatively influenced the response at the lowest concentrations. By introducing the background electrolyte the lower detection limit was one order of magnitude higher in comparison to pure lead(II) nitrate solutions. The change in *LDL* is primarily dictated by the selectivity coefficient for Pb^{2+} over K^+ for Pb^{2+}-ISEs ($\log K^{\mathrm{pot}}_{\mathrm{Pb^{2+},K^+}} = -5.7 \pm 0.6$). None the less, the useful concentration range was broad enough to consider the applicability of the sensor in measurements of lead in diluted samples. Figure 15 presents changes of formal potential at open circuit in 10^{-5} mol dm^{-3} Pb^{2+} after each conditioning cycle: A) for pure, unbuffered solutions of lead(II) nitrate, and B) for lead(II) nitrate with constant potassium nitrate background electrolyte (including up to four recovery cycles). After the second cycle, when the electrode was for the first time in contact with Pb^{2+}, the potential at $pPb^{2+} = 5$ significantly dropped. With the next cycles the potential gradually increased, being established at an approximately constant value when no effect of lowering of the detection limit was anymore observed. It is clear that unconditioned membranes exhibit deviation in formal potential, and only when the membrane is well conditioned the $E°$ ought to be stable. After the recovery process in pure solution, irregular deviation of potential at $pPb^{2+} = 5$ was observed. It can be attributed to the exchange of Na^+ that has accumulated in the PVC membrane.

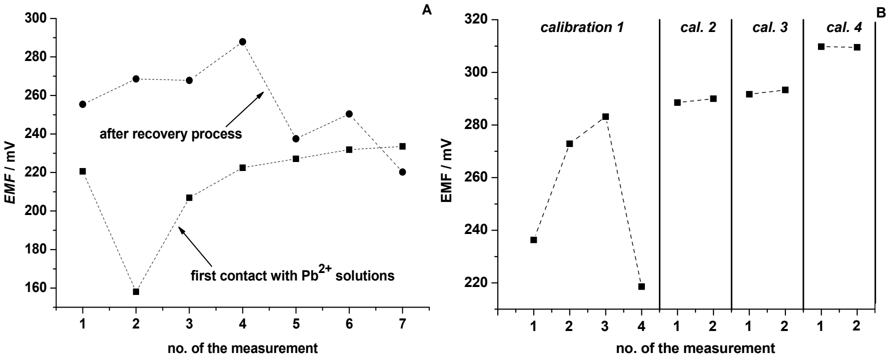

Figure 15. Changes of open circuit potential values ($E°$) in 10^{-5} mol dm^{-3} Pb^{2+} after each conditioning cycle: A) for pure, unbuffered solutions of lead(II) nitrate (-■- first contact with lead solutions and -●- after the recovery process), and B) for lead(II) nitrate with constant potassium nitrate background electrolyte (including up to four recovery cycles called *calibration1, cal.2, cal.3, cal.4*, vertical lines are as an indication of performed recovery process).

Figure 15 B presents consecutive measurements consisting of conditioning cycles to obtain response at low concentrations (*LDL*~ 10^{-8} mol dm^{-3} Pb^{2+}). When the response was lost at lowest concentration of Pb^{2+}, the recovery process was applied and the measurement was run again (four in total). Although with each recovery process an upward change of $E°$ was observed, the formal potential of the electrodes when reaching the desired low detection limit during one measurement did not change significantly, and lasted for at least two conditioning cycles. From three consecutive measurements the formal potential shift between two calibration procedures based on concentration and time dependent conditioning was determined to be 1.1 ± 0.6 mV. This allowed preparation of the calibration curve and immediate analysis of the sample.

The effects of conditioning of the ion-selective membrane on the low detection limit are summarized in Figure 16. Obtaining a low detection limit by controlled conditioning of the membrane depends not only on the membrane but also on the conditioning solution. When using solutions with higher ionic strength, the lower detection limit was obtained faster, but it lasted shorter than in the case of pure solutions of $Pb(NO_3)_2$.

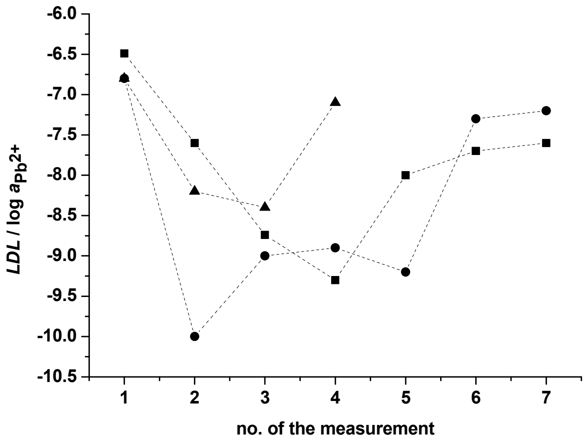

Figure 16. Low detection limit of solid-contact Pb^{2+}-selective electrode as a function of the number of conditioning cycles performed (-■- pure, unbuffered solutions of $Pb(NO_3)_2$, -●- pure, unbuffered solutions of $Pb(NO_3)_2$ after the recovery process, and -▲- unbuffered solutions of $Pb(NO_3)_2$ with constant background electrolyte 10^{-3} mol dm^{-3} KNO_3).

None the less, the effect is limited by concentration and time of conditioning, and the lowering of the detection limit was obtained only for insufficiently conditioned membranes. When membranes were saturated with Pb^{2+} the sensitivity toward the primary ion was much worse. All the *LDLs* and slopes values calculated from measurements done using the conditioning protocol are collected in Table 2.

Table 2. Low detection limits (*LDL*) and slopes of the responses of solid-contact Pb^{2+}-ISEs when applying conditioning protocol to lower the detection limit (three cases investigated: pure, unbuffered solutions of $Pb(NO_3)_2$ (first time in contact with the primary ion), pure, unbuffered solutions of $Pb(NO_3)_2$ after recovery process, and unbuffered solutions of $Pb(NO_3)_2$ with constant background electrolyte 10^{-3} mol dm^{-3} KNO_3. *Super-Nernstian response.

No.	Pure, unbuffered $Pb(NO_3)_2$ solutions (Figure 12 A)		After recovery process (Figure 12 B)		Unbuffered $Pb(NO_3)_2$ solutions, const. 10^{-3} mol dm^{-3} KNO_3 (Figure 14)	
	LDL [log$a_{Pb^{2+}}$]	*Slope* mV dec^{-1}	*LDL* [log$a_{Pb^{2+}}$]	*Slope* mV dec^{-1}	*LDL* [log$a_{Pb^{2+}}$]	*Slope* mV dec^{-1}
1	–6.5*	20.7	–6.8*	24.7	–6.8*	25.7
2	–7.6*	25.5	–10.0	27.7	–8.2*	33.0
3	–8.7	30.9	–9.0	26.5	–8.4	27.5
4	–9.3	26.6	–8.9	26.9	–7.1	22.5
5	–8.0	28.1	–9.2	26.2		
6	–7.7	27.1	–7.3	26.6		
7	–7.6	26.1	–7.2	26.0		

The renewable response was obtained with solid-contact Pb^{2+}-ISEs by using a strict protocol of electrode conditioning allowing determination of concentrations which are not usually reachable for ISEs without any modifications. Together with the measurement protocol the solid state design of the electrode allowed partially reversing the ion flux (from the membrane to the recovery solution) which resulted in renewable response at extremely low concentrations of primary ion. By applying a fairly diluted conditioning solution containing Na_2EDTA, the release of Pb^{2+} from the membrane was possible (recovery process). The recovery of ultra low detection limit of solid-contact Pb^{2+}-ISEs allowed further investigation of their application in the determination of Pb^{2+} in prepared samples.

8.5 Time-dependant adsorption of analyte on Pb^{2+} solid-state (PbS/Ag_2S) membrane electrodes for lowering of the detection limit

Although recent research on *LDL* concentrates exclusively on plastic membranes, the solid-state ISEs offer an advantage of simplicity that was overlooked. Thus, a parallel investigation of lowering the detection of solid-state PbS/Ag_2S (6:4, mol:mol) electrodes to the one for solid-contact Pb^{2+}-ISEs was performed (***Paper IV***). As described in chapter 5, the prime cause of poor performance of solid-state membrane electrodes is connected to parasitic processes occurring at the membrane surface.

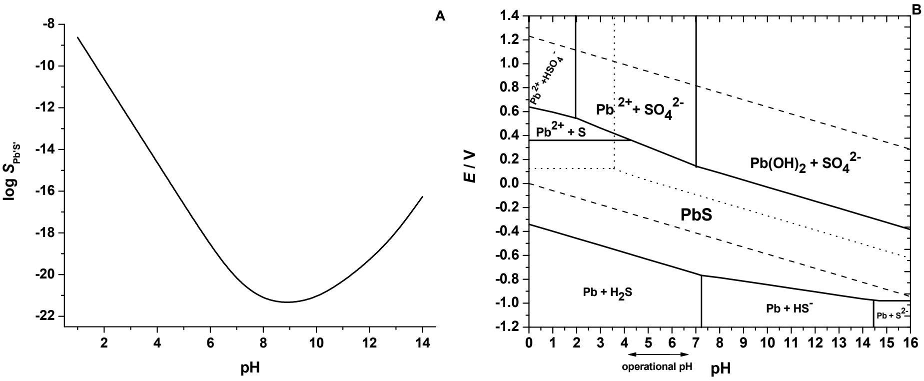

Figure 17. PbS/Ag_2S membrane: A) Conditional solubility products constant at various pH taking into account side reactions coefficients of Pb^{2+} and S^{2-}, B) E-pH diagram of Pb-S-H_2O system at 25 °C. (—) $[Pb^{2+}] = 10^{-1}$ mol dm^{-3}, $[HSO_4^-] = [SO_4^{2-}] = [H_2S] = [HS^-] = [S^{2-}] = 10^{-1}$ mol dm^{-3}, (· · ·) $[Pb^{2+}] = 10^{-9}$ mol dm^{-3}, $[HSO_4^-] = [SO_4^{2-}] = [H_2S] = [HS^-] = [S^{2-}] = 10^{-1}$ mol dm^{-3}, (- - -) potential stability window for water at 25 °C. The arrow shows pH range in unbuffered solutions.

Generally, a predominant side reaction in solid-state PbS/Ag_2S membrane electrodes was found to be due to solution pH. This is shown by conditional solubility of lead sulfide shown in Figure 17 A. Minimum solubility of lead sulfide is obtained in the pH range 8-

10. In this region the effect of hydrogen and hydroxide ions on solubility of PbS is small, and only 10^{-10} to $10^{-10.5}$ mol dm^{-3} PbS is dissolved. Furthermore, lead sulfide undergoes pH dependent reduction/oxidation reactions that can change the analytical concentration of Pb^{2+}. The electrical potential-pH (Pourbaix) diagram for the Pb-S-H_2O system (Figure 17 B) helps to illustrate possible redox effects [102]. For this reason the lines corresponding to lead activity in the solution of 10^{-1} and 10^{-9} mol dm^{-3}, are marked in the diagram. From the Pourbaix diagram it can be seen that the shift in the potential values (versus NHE) under which the lead sulfide oxidizes is strictly connected to the concentration of lead in the solution. Less concentrated solution of lead promotes oxidation at lower potential values, a fact well known for sparingly soluble sulfides [200]. In this case the operative potential values are from –0.38 V to –0.18 V (taken from Figure 19 B and recalculated for the NHE) and the pH range unbuffered solutions was $4 < pH < 7$, indicated by arrow in Figure 17 B. The oxidative dissolution of lead sulfide results in the formation of soluble sulfates coupled with increased lead ion concentration at the membrane surface, according to the reaction in eq. 21:

$$PbS + 4H_2O \rightarrow Pb^{2+} + SO_4^{2-} + 8H^+ + 8e^- \qquad (21)$$

The above process is reflected by the apparent deterioration of the detection limit. In view of Figure 17 to minimize the influence of parasitic effects it was found advantageous to remove oxygen, for example by purging argon and/or to decrease the redox potential of the solutions without affecting concentrations of free lead ion, for example by addition of small amounts, less than 2 mg dm^{-3}, of ascorbic acid [78, 82].

An excellent way to get information about the performance of ISEs at low concentrations is metal titration [94]. Free lead ion activities were calculated after every addition of Tiron from the pH values recorded during the titration and a total concentration of complexing agent added to the solution of lead(II) nitrate. The protonation constants used in the calculations were: $\log K_{\mathrm{HL}}^{\mathrm{H,L}} = 12.7$, $\log K_{\mathrm{HL_2}}^{\mathrm{H,L}} = 7.7$ for H_2Tiron, and the stability constants $\log K_{\mathrm{PbL}}^{\mathrm{Pb,L}} = 11.95$, $\log K_{\mathrm{PbL_2}}^{\mathrm{Pb,L}} = 6.35$ [198]. Results of the metal titration method are presented in Figure 18 A. In this experiment the solid-state electrode exhibits a linear response in the low range of lead activity, from 10^{-5} to $10^{-8.1}$ mol dm^{-3}. The slope of the calibration curve in the entire activity range was 27.8 mV dec^{-1}. Use of Tiron as a complexing agent allowed to obtain linearity of the calibration curve down to $pPb^{2+} = 8.1$.

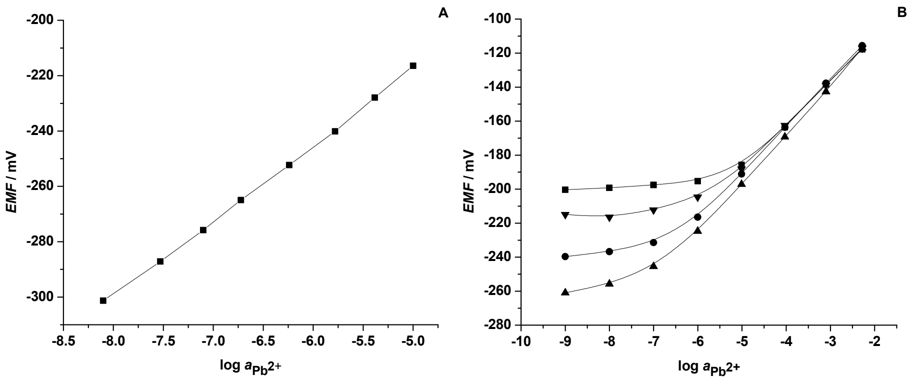

Figure 18. Solid-state PbS/Ag_2S membrane Pb^{2+}-ISE: A) calibration curve obtained in well controlled conditions by titration of Pb^{2+} in Tris buffer (pH 8) with Tiron, B) influence of stirring and purging the unbuffered solution with argon on lowering the detection limit: (■) calibration without stirring and purging argon, (▼) purging argon, (●) stirring, (▲) purging argon while stirring.

This shows that by minimizing interferences the solid-state lead-selective electrode is closer to the theoretical value of the low detection limit indicated by the solubility product of lead sulfide ($-\log S = 13.3$, Table 3). However in this method the free activity of Pb^{2+} is supported by relatively high total concentration of this ion, so, as in the case of ionic buffers, its analytical value is rather limited.

Table 3. Solubility products and solubilities of the solid-state membrane components without considering side reactions [200].

Component of the solid-state membrane	$-\log Kso_{\mathrm{M_nS}}$	Solubility ($-\log S$) of M_nS
PbS	26.6	13.3
Ag_2S	49.2	16.6

Furthermore, it was found that an extrathermodynamic factor, such as stirring, brings favourable effects. However, we did not dedicate a special study, except of a very practical selector: with or without stirring. The potentiometric behaviour of a Pb^{2+} solid-state membrane ISE in the unbuffered solutions of the main ion is shown in Figure 18 B. By investigating various conditions of the calibration procedure it was concluded that stirring and purging the sample solution with argon exert an influence on the performance of the electrode. The slope calculated from the linear part of the calibration curve for all applied conditions was close to Nernstian. As expected, the lowest detection limit was obtained for calibration when purging with argon and solution stirring were applied, and was $10^{-7.1}$ mol dm^{-3} with a slope of 28.9 mV dec^{-1}. Stirring enhanced transport and facilitated removal of reactants from/to the solid membrane as well as removal of dissolved oxygen by purging the sample solution with argon. In comparison with the calibration, without stirring and purging argon the detection limit was lowered by about two orders of magnitude.

A new concept (kinetic calibration) of measuring of lead(II) emerged with the investigation of solid-state Pb^{2+}-ISEs under various conditions. It takes advantage of concentration-dependent potential changes over time after the same pre-treatment of the Pb^{2+}-ISE membranes. This was achieved by a strict protocol of polishing, titration with sodium sulfide and subsequent soaking in sodium sulfide. The kinetic curves of the investigated activities of the lead ion are presented in Figure 19 A. Each time the solid-state membrane electrode was bathed in the solution with extremely low Pb^{2+} activities, according to the above described titration procedure. Subsequently, kinetic curves were recorded after placing the electrodes in the calibrating solutions. The concentrations of lead(II) in the most diluted solutions were checked by ICP-MS. For 10^{-9} and 10^{-10} mol dm^{-3} of lead(II) nitrate the lead concentrations measured by ICP-MS were $10^{-9.01}$ and $10^{-10.1}$ mol dm^{-3}, respectively.

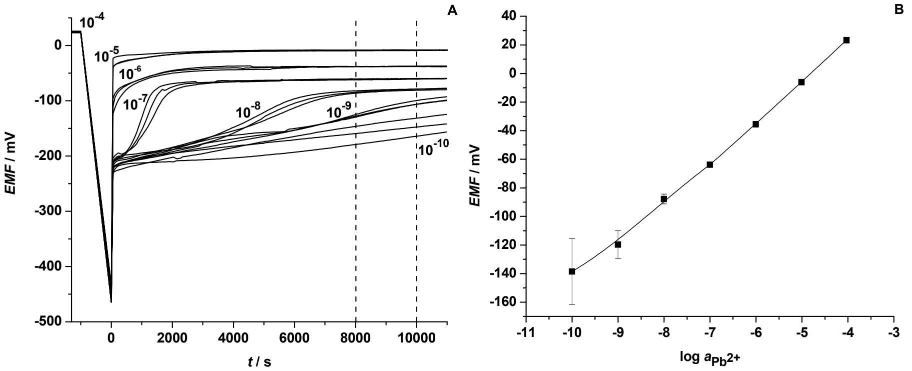

Figure 19. Solid-state PbS/Ag_2S membrane electrode: A) kinetic curves recorded at different lead ion activities. The dashed lines show the time interval where data was collected for the slope calculation, B) calibration curve obtained from the kinetic calibration procedure. The error bars show the uncertainties for three measurements.

It was observed that the kinetic curves recorded in higher activity of lead ion (10^{-5}, 10^{-6} mol dm^{-3} Pb^{2+}) were reaching stable potential after a short time while the kinetic curves recorded in diluted solutions (in the range 10^{-9} to 10^{-10} mol dm^{-3} Pb^{2+}) indicate that a stable potential (drift less than 0.02 mV min^{-1}) was not attained. None the less, from the range from 8000 to 10 000 s a clear distinction between each curve for the particular concentration was observed. This effect can be attributed to concentration and time dependent adsorption [78]. By averaging the potential values (arithmetical mean) from the range of 8000-10000 s for three consecutive kinetic curves of each activity of Pb^{2+} the calibration curve (with marked uncertainty) is presented in Figure 19 B. The sensitivity was observed in a broad range of lead activity with close to a Nernstian slope of 29.3 mV dec^{-1} and the detection limit $10^{-8.0}$ mol dm^{-3}.

Since the concentration-dependent adsorption of analyte at the membrane surface is a relatively slow process; the time the measurement takes is still a factor which limits the applicability of this method in routine environmental analysis. Therefore a much faster, better controlled and more reliable method for PbS/Ag_2S membrane electrodes was needed for measurements of Pb^{2+} at low concentrations.

8.6 Tuned galvanostatic polarization method of Pb^{2+} solid-state electrodes for lowering of the detection limit

When applying current controlled measurements with solid-state lead-selective electrodes, the tuned galvanostatic polarization method for solid-state lead-selective was developed (***Paper V***). The lowering of the detection limit of a solid-state lead-selective electrode applying galvanostatic polarization was possible by decreasing the oxidation of the membrane components in aqueous sample solutions. Figure 20 presents the oxidation properties of lead sulphide (the main component of the solid-state ISEs) as a function of pH at various potential values (vs. NHE).

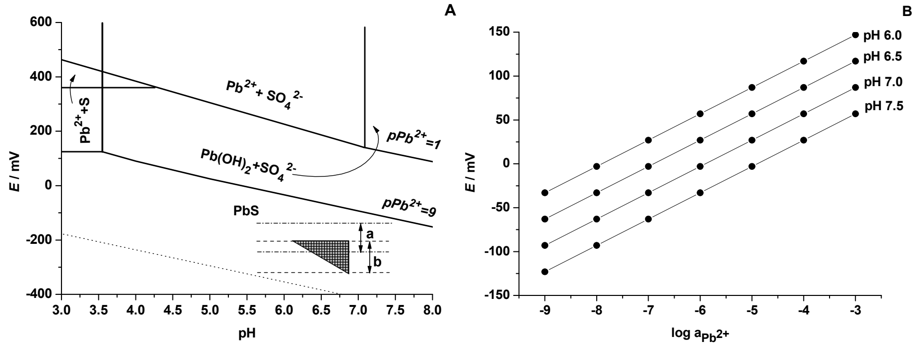

Figure 20. A) E-pH diagram of Pb-S-H_2O system at 25°C, (—) [Pb^{2+}]= 10^{-1} or 10^{-9} mol dm^{-3}, [SO_4^{2-}]=[HSO_4^-]=[H_2S]=[HS^-]=[S^{2-}]= 10^{-1} mol dm^{-3}, (···) potential stability for water at 25°C, (a) potential range of zero current measurement, (b) potential range when galvanostatic polarization is applied, and checked triangle: analytical potential range when galvanostatic polarization is applied in unbuffered solutions, B) Influence of lead activity in the solution on the oxidation potential of Pb-S-H_2O system at 25°C at various pH.

The chosen pH range (from 3 to 8) refers to the actual measurement conditions. Without special precautions, electrodes may operate in an unsafe range of potential, for example in an oxidizing environment. The oxidation initiates dissolution of the membrane components and results in the release of Pb^{2+} which contaminates the sample, thus changing the initial lead activity. Operating at higher pH may result in further binding of lead to lead(II) hydroxide, eq. 22:

$$Pb^{2+} + 2OH^{-} \rightarrow Pb(OH)^{+} + OH^{-} \rightarrow Pb(OH)_{2\downarrow} \qquad (22)$$

The checked triangle marked in Figure 20 A refers to the actual measurement conditions at 10^{-6} to 10^{-9} mol dm^{-3} Pb^{2+}: (b) indicates the potential range at which the electrode is operating under galvanostatic polarization, and (a) corresponds to the potential range of the measurement taken without applying external current. It is clear that, when polarized by cathodic current, the electrode is working in less oxidizing conditions than during measurement at zero current potentiometry. For a better understanding, the oxidation potential of the PbS as a function of various lead activities in the sample solution for a narrow pH range (6.0-7.5) is presented in Figure 20 B. For various pH, the oxidation behaviour is similar and strongly dependent on the log $a_{\mathrm{Pb(II)}}$ in the sample solution. Since we address measurements at low lead activity (10^{-7} to 10^{-9} mol dm^{-3} Pb^{2+}), the potential at which the electrode undergoes oxidation is the lowest, and unsafely close to our operational conditions. By passing external current we decrease the oxidation processes at the membrane surface, and lowering of the detection limit becomes possible.

The procedure used for obtaining the low detection limit with the chronopotentiometric method is shown in Figure 21. After immersion, the electrode system was kept in the solution containing the target ion until the potential stabilized, after which the measurements were run. The measurement was divided into three parts, each lasting for 60s. During the first stage the open circuit potential was recorded. This stage promotes further stabilization of the potential readouts before applying specific current densities to the solid-state membrane. The next stage was to polarize the membrane with a cathodic current, whose density was specific for each lead activity. Immediately after turning the current on, an Ohmic drop to more negative potentials was observed, followed by a polarization curve. When the current was switched off, an Ohmic drop to more positive potentials occurred first and then the potential started to relax back to the initial value. As an analytically relevant signal, the potential was sampled after 0.4 s after turning the current off. By this time, the positive Ohmic drop was well over, so the signal refers to the beginning of the relaxation process. The linearization of the calibration curve was achieved by tuning the current density as a function of the activity of the primary ion, promoting a change in the potential of about 30 mV per decade of $a_{\mathrm{Pb(II)}}$. For all the cases, incomplete relaxation was observed during the last stage. Obviously, 60s is not enough for complete relaxation of the potential, and therefore the next run was started after a delay of ten minutes when the potential was stable enough to run the next measurement. To lower the effects of the Ohmic drop, a relatively high activity of KNO_3 was used as background electrolyte.

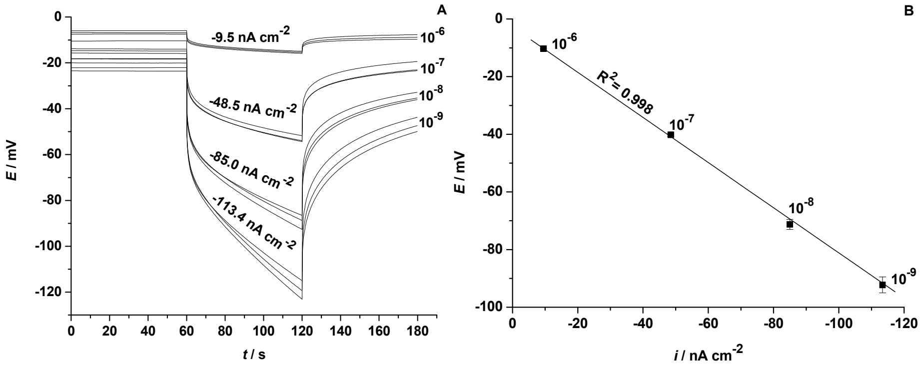

Figure 21. A) chronopotentiometric curves (three consecutive measurements at each lead activity) illustrating the tuned glavanostatic polarization method for a solid-state lead-selective electrode, B) dependence of the potential of polarized solid-state Pb(II) electrode on the current density at different lead activities (illustrating the linearization of response in diluted solutions).

From Figure 21 A it can be seen that relatively high current densities were used while polarizing the solid-state membrane compared to previously proposed current densities for solvent polymeric membranes [135]. This allowed shortening the time of the measurement. Furthermore, for each lead activity the measurements were performed three times with a one-day delay between the calibrations, and the repeatability of the chronopotentiometric curves was satisfactory, as shown in Figure 21 B. Good linearity (R^2= 0.998) suggests that the polarization is proportional to the tuned current densities. This fact indicates the possibility of lowering the detection limit, and thus determining the analyte at low concentrations.

For comparison, two different approaches were investigated: with and without applied current. In Figure 22 A, a potentiometric calibration curve is presented for: (a) zero current potentiometry, and (b) chronopotentiometry. In the range from 10^{-3} to 10^{-5} mol dm^{-3}, calibration curves were obtained for both cases without applied current. Both curves were characterized with Nernstian slope, and thus there was no need to apply external current. Without external current, the electrode slope between pPb^{2+} 5 and 6 was sub-Nernstian: 24.8 mV dec^{-1}. Since the lack of a Nernstian response was observed in a lower activity range, the electrodes were polarized to extend the linearity of the calibration curve.

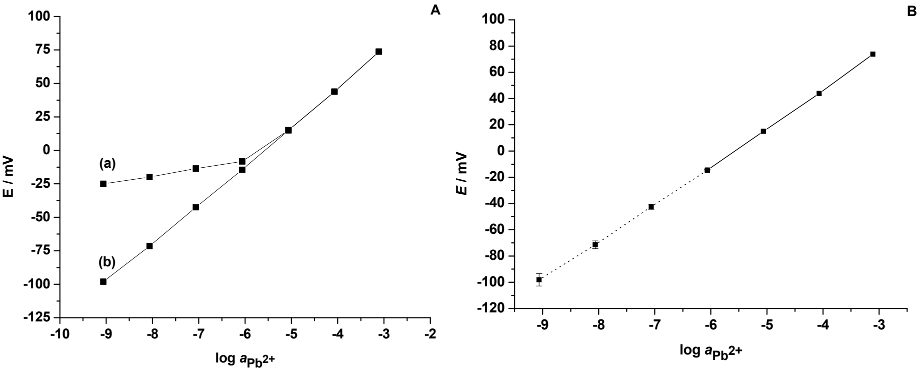

Figure 22. A) calibration curve of ISE-Pb^{2+} in unbuffered solutions of lead(II) nitrate: (a) in zero current potentiometric mode, and (b) in chronopotentiometric mode, B) calibration curve obtained by tuned galvanostatic polarization. The error bars correspond to standard deviations obtained in three consecutive measurements.

Applying the galvanostatic polarization method made it possible to decrease the sensitivity to $pPb^{2+}= 9$ with a slope along the entire calibration curve (10^{-3}-10^{-9} mol dm^{-3} Pb^{2+}) equal to 28.9 mV dec^{-1}. Furthermore, potential uncertainties at low activities between different measurements were investigated and determined not to exceed 3 mV. The calibration line composed from three consecutive measurements with standard deviation marked for each calibration point was prepared on Figure 22 B. The entire calibration curve was characterized with a 28.9 mV dec^{-1} slope and the detection limit of $pPb^{2+}= 9$. The standard deviation from the trend line for 10^{-7}, 10^{-8}, 10^{-9} mol dm^{-3} solution was 1.2 mV, 3.0 mV, 4.7 mV, respectively. An improvement in the detection limit of three orders of magnitude was thus obtained for the chronopotentiometric calibration method over classical potentiometry.

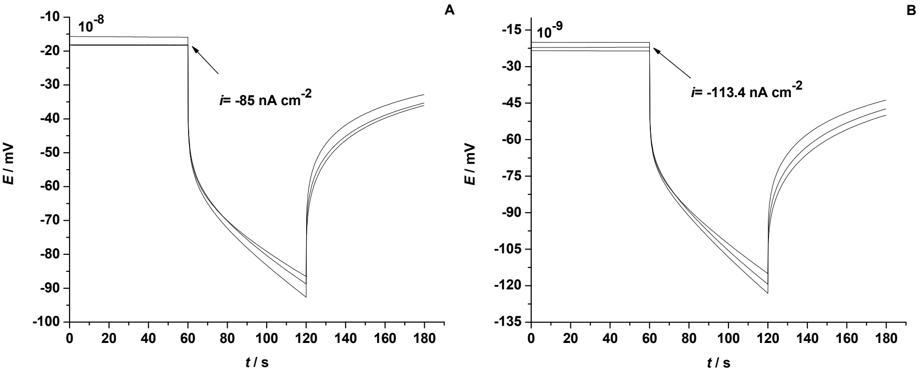

Figure 23. Repeatability of polarization curves recorded at specific current densities for Pb^{2+} activities of A) 10^{-8} mol dm^{-3} and B) 10^{-9} mol dm^{-3}.

The repeatability of the chronopotentiometric curves for lead activities of 10^{-8} mol dm^{-3} and 10^{-9} mol dm^{-3} is shown in Figures 23 A and B, respectively. To avoid undesirable uncertainty related to the preparation of the samples, all the measurements were performed using the same stock solution of 10^{-6} mol dm^{-3} $Pb(NO_3)_2$.

Lowering the detection limit of solid-state lead-selective electrodes by using the tuned galvanostatic polarization method was achieved. By applying current which facilitates the membrane to work in less oxidizing conditions the detection limit can be drastically improved. Good sensitivity with a Nernstian slope down to 10^{-9} mol dm^{-3} was attained. The advantages, such as the short time of analysis, repeatability of the results, ease of the operations, together with the robustness of solid-state membranes, provide excellent opportunities to measure reliably in the nanomolar concentration range. Therefore the sensor was applied in the determination of Pb^{2+} in various samples.

8.7 Influence of pH on the analysis of Pb^{2+} in unbuffered samples

Except for the influence of pH on the solubility of the PbS/Ag_2S membrane and oxidation/reduction effects, pH has additional meaning in terms of free lead concentration in the sample solutions (***Paper VI***). Lead ion undergoes hydrolysis in water solutions to a range of hydroxyl complexes. The speciation of lead in aqueous solutions is strongly pH-dependent, so the ratios between the free and the bound form of Pb^{2+} were estimated through the side reaction coefficient ($\alpha_{(PbOH_x)}$) for lead(II) with the hydroxyl group at various pH.

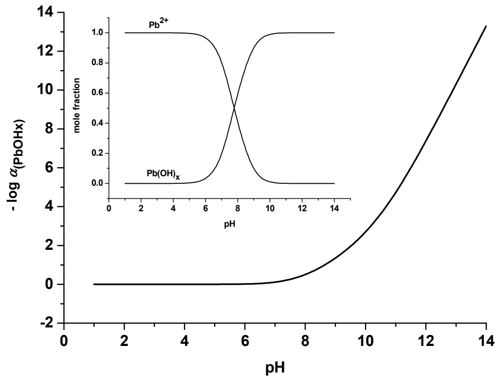

Figure 24. Logarithmic values of $\alpha_{(PbOH_x)}$ for Pb^{2+} side reaction coefficient with OH^- with molar fraction of free and bound lead(II) at various pH, using equilibrium constants [198].

The results are shown in Figure 24 where, in the pH range between 1 and 4 ($\alpha_{(PbOH_x)}$= 1), 100% of ionized lead is present. The formation of hydroxyl complexes starts to occur at pH 5 ($\alpha_{(PbOH_x)}$>1) followed by a significant decrease of Pb^{2+} already at pH 7, and finally at pH 9 lead is mostly present in the complexed form.

The speciation of lead solutions at various pH would indicate constant monitoring and adjustment of pH during the measurements. However in environmental analysis a direct determination is often required, so changes in pH and the composition of the sample are not recommended. Moreover, the toxicity of lead(II) is connected to its speciation [201]. Therefore in environmental samples the concentration of free form has to be monitored, keeping in mind that the pH at environmental conditions is biased; therefore the $[Pb^{2+}]$ is biased too. Thus, a simultaneous measurement of pH and Pb^{2+} may enable free and complexed forms to be estimated.

To investigate the impact of unbuffered solutions on the free lead activity, a PbS/Ag_2S membrane electrode was investigated at various $Pb(NO_3)_2$ concentrations. The solid-state electrode was immersed in 10^{-5} mol dm^{-3} $Pb(NO_3)_2$ containing 10^{-3} mol dm^{-3} KNO_3 background electrolyte. Subsequently, using a glass electrode the pH was measured after every tenfold dilution, down to 10^{-9} mol dm^{-3} Pb^{2+} retaining the same background electrolyte concentration. The calculations of the free and bound form of lead are shown in Table 4.

Table 4. Influence of side reactions of Pb^{2+} with OH^- and NO_3^- and solubility of PbS on free Pb^{2+} activity ($\log a_{Pb^{2+}}$) in calibration solutions of lead (c_{Pb}) with background of 10^{-3} mol dm^{-3} KNO_3.[a] For solid-contact electrode in 10^{-9} mol dm^{-3}, $\log a_{Pb^{2+}} = -9.042$.

c_{Pb} [mol dm^{-3}]	pH	$\alpha_{(PbOH_x)}$	% of c_{Pb} in $PbOH_x$, PbL_n	$\log K'_{so}$	$\log a_{Pb^{2+}}$
10^{-5}	5.73	1.009	0.84	–18.07	–5.063
10^{-6}	5.88	1.012	1.19	–18.36	–6.061
10^{-7}	6.03	1.017	1.67	–18.64	–7.062
10^{-8}	6.20	1.025	2.45	–18.96	–8.062
10^{-9}	6.37	1.037	3.58	–19.27	–9.149*

[a] where $\alpha_{(PbOH_x)}$ is side reaction coefficient for OH^-; percentage of bound Pb^{2+}; conditional solubility of PbS ($\log K'_{so}$)

From the pH of each lead solution, the side reaction coefficient for lead with the hydroxyl group was established ($\alpha_{(PbOH_x)}$). Additionally, taking into account the side reactions for Pb^{2+} with NO_3^- ($\log K^{Pb,L}_{PbL} = 0.3$, $K^{Pb,L}_{PbL_2} = 0.1$ [202]) the percentage of bound lead to hydroxides and nitrates was obtained. At the two lowest $Pb(NO_3)_2$ concentrations a significant loss of free lead concentration, over 2%, was generated. Furthermore, the PbS/Ag_2S membrane partially releases Pb^{2+} due to the solubility of the PbS/Ag_2S membrane at various pH. The conditional solubility of the PbS/Ag_2S membrane ($\log K'_{so}$) results in a discharge of ionized lead, approximately 10^{-10} mol dm^{-3} Pb^{2+} which limits the applicability of the solid-state membrane down to 10^{-9} mol dm^{-3} Pb^{2+} in the sample solutions. Finally, including all factors affecting the free lead concentration together with the corrections for the higher ionic strength (activity coefficient calculated using the Debye-Hückel approximation), the final activity of Pb^{2+} was generated ($\log a_{Pb^{2+}}$). The direct determination of Pb^{2+} in the environmental sample in the analytical range between 10^{-6} and 10^{-8} $Pb(NO_3)_2$ was possible due to an acceptable operational pH range of the PbS/Ag_2S electrode (pH between 3.0 and 6.5) and the insignificant influence of the membrane solubility.

8.8 Determination of Pb^{2+} in synthetic samples by solid-contact and solid-state Pb^{2+}-ISEs

Determination of lead(II) was performed by two separate methods, previously described in the text: time and concentration dependent conditioning procedure to recover the *LDL* for solid-contact electrodes (***Paper III***) and tuned galvanostatic polarization method for solid-state PbS/Ag_2S membrane electrodes (***Paper V***). In both cases the measurement done in potentiometric mode was confirmed by the analysis done with ICP-MS.

Table 5. Observed electrode slopes and selectivity coefficients obtained according to separate solution method for solid-contact Pb^{2+}-ISE, slope between $-\log a_{Pb(II)}$ 2.3 and 4.0 was 29.2 ± 1.9 mV dec^{-1} (the standard deviation from the measurement was obtained from three identical electrodes). All the measurements were performed at pH close to 4.

j	*Slope* / mV dec^{-1}	$-\log a_j$ range for slope calculation	$\log K^{pot}_{Pb^{2+},j}$
Ca^{2+}	30.5 ± 1.3	1.5 - 3.1	–4.9 ± 0.9
K^+	42.6 ± 0.7	1.1 - 3.0	–5.7 ± 0.6
Na^+	33.9 ± 0.7	1.1 - 3.0	–5.4 ± 0.5
Zn^{2+}	27.1 ± 1.6	2.3 - 4.0	–7.4 ± 0.7
Cd^{2+}	26.1 ± 1.0	2.3 - 4.0	–3.0 ± 0.3
Cu^{2+}	26.8 ± 0.6	2.3 - 4.0	–2.5 ± 0.4

Considering solid-contact Pb^{2+}-ISEs for measurements in the sample solutions, selectivity toward primary ion was inspected. The selectivity for solid-contact electrodes was obtained using separate solution method (SSM) and presented as selectivity coefficients in Table 5. Significantly better selectivity coefficients for Pb^{2+} over K^+, Na^+, and Zn^{2+} were attained than in the previously inspected conventional type of Pb^{2+}-ISEs based on lead ionophore IV [44]. Moreover, the obtained selectivity indicates that the electrodes are more selective to lead than to any of the inspected interfering ions. Together with the small shifts of $E°$, it indicates the possibility to apply this sensor in order to determine lead in various samples.

Subsequently, the analysis of the synthetic Pb^{2+} sample (4.0×10^{-8} mol dm^{-3} $Pb(NO_3)_2$ + 10^{-3} mol dm^{-3} KNO_3) was performed. The analysis was performed at non-equilibrium conditions (after recovery of lower detection limit) in two potentiometric configurations: a direct determination taking readout from the calibration curve (Figure 25 A) and the single standard addition method (Figure 25 B).

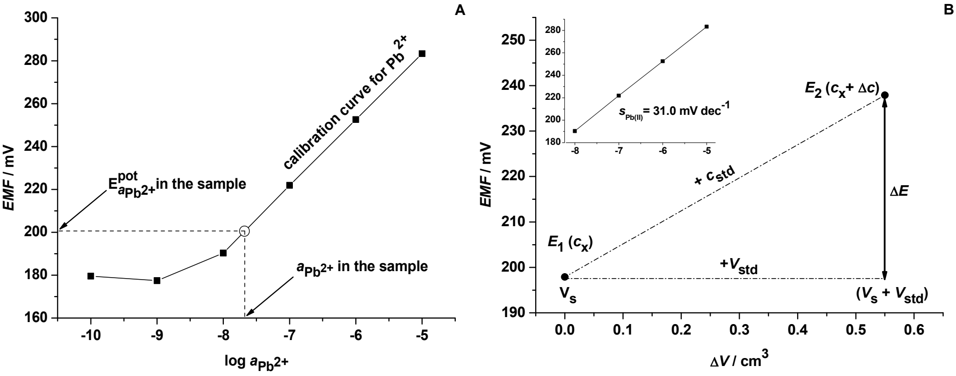

Figure 25. Analytical procedure of lead determination in the synthetic sample (4.0×10^{-8} mol dm^{-3} $Pb(NO_3)_2$, 10^{-3} mol dm^{-3} KNO_3) for solid-state lead-selective electrodes: A) direct ionized lead determination from Pb^{2+} calibration curve and B) single standard addition method (SAM), where $E_1(c_x)$ is potential of the solid-state electrode in the synthetic sample, $E_2(c_x+\Delta c)$ is potential of the solid-state electrode after standard addition, c_{std} is concentration of the standard solution, V_s is volume of the sample, V_{std} is volume of the standard. Insert: Pb^{2+} calibration curve done prior to the determination, slope used to calculate ionized lead concentration in the synthetic sample.

Taking into account that the synthetic sample was indeed within the analytical range of the electrode and the selectivity of Pb^{2+}-ISEs was sufficient enough, after the recovery process the determination could be performed. When applying the conditioning-based calibration, solid-contact lead-selective electrodes obeyed the Nernst equation down to $pPb^{2+}= 8$ with a slope of 30.5 mV dec^{-1}. Subsequently, electrodes were immersed in synthetic sample solution and the potential readout after 5 minutes while stirring was used to calculate the activity of Pb^{2+} in the synthetic sample. The uncertainty was calculated for two electrodes out of two measurements. The Pb^{2+} activity was determined to be

pPb^{2+}= 7.64 ± 0.11. Additionally, the single standard addition method was performed. This method has significant advantages, for example the elimination of the formal potential of the electrode ($E°$) [203]. As it was reported, $E°$ of the solid-state Pb^{2+}-selective electrode shifts with every measurement, so the application of this method is convincingly justified. Knowing the slope of the calibration curve (newly prepared calibration curve, 31.0 mV dec^{-1}) and that the concentration of the synthetic sample was within the response range of the electrode, the determination was performed. The *EMF* of the electrode was measured in 50 cm^3 of the sample (stirred solution) and the potential readout ($E_1(c_x)$) was taken after 5 minutes. When adding 0.55 cm^3 (V_{std}) of 8.7×10^{-5} mol dm^{-3} $Pb(NO_3)_2$ (c_{std}) to 50 cm^3 (V_s) of synthetic sample, the *EMF* data was recorded (stirred solution) for another 5 minutes ($E_2(c_x+\Delta c)$). Knowing the slope of the Pb^{2+}-calibration curve ($s_{Pb(II)}$), volume (V_s+V_{std}) and concentration of Pb^{2+} standard solution, and the potential difference (ΔE) after addition of standard solution, the Pb^{2+} activity in the synthetic sample was calculated. The uncertainty was obtained for two electrodes out of two measurements. The Pb^{2+} activity was determined to be pPb^{2+}= 7.27 ± 0.07. The activity of lead in the synthetic sample done in potentiometric modes was compared using inductively coupled plasma mass spectrometry. The value of the total lead concentration obtained by ICP-MS measurement was pPb= 7.34. To summarize, solid-state lead-selective electrodes based on polybenzopyrene doped with eriochrome black T and PVC membrane (lead ionophore IV) were successfully applied in the determination of Pb^{2+} in synthetic sample although the determination was performed at non-equilibrium conditions. The single standard addition method in comparison to ICP-MS analysis was performed with satisfactory accuracy. A more reliable way when measuring with a solid-contact Pb^{2+}-electrode is to apply the single standard addition method to eliminate any possible drift of $E°$.

Furthermore, the tuned galvanostatic polarization (TGP) method was used with solid-state PbS/Ag_2S membrane electrodes to measure the concentration of Pb^{2+} in synthetic sample. Since, in this particular determination sample contain only $Pb(NO_3)_2$ and 10^{-3} mol dm^{-3} KNO_3 the aspect of the selectivity toward other ions was neglected. As for environmental samples the problem of sufficient selectivity to primary ion over interfering ions arises. Especially in case of PbS/Ag_2S membranes, the direct correlation between low detection limit and the selectivity needs to be taken into account as the response of solid-state membranes may suffer from the presence of interfering ions [27, 173]. The analytical procedure of lead determination in a synthetic sample is shown in Figures 26 A and B. A calibration curve in the range of 10^{-7} to 10^{-9} mol dm^{-3} Pb^{2+} was obtained by applying tuned current densities to a solid-state membrane for each lead activity. In the case of the samples, there are two unknowns: the activity of the target analyte and the current density that is optimal for that particular activity. However, it has been shown previously how to deal with this matter [135, 136].

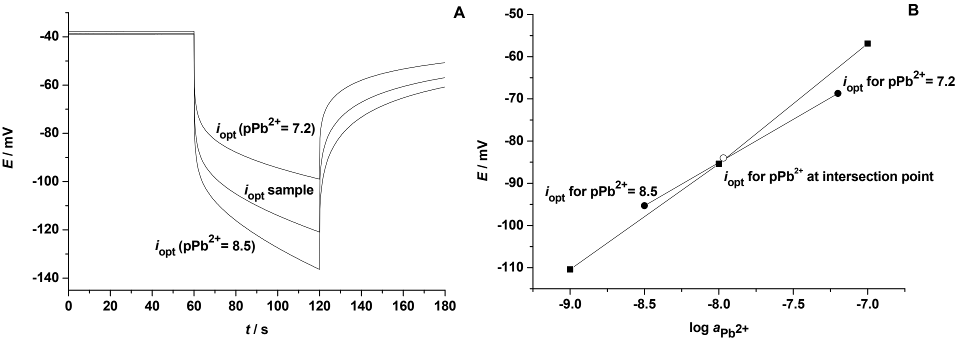

Figure 26. Analytical procedure of lead determination in synthetic sample: A) Three chronopotentiometric curves recorded with the two arbitrarily chosen current densities corresponding to pPb=7.2 and 8.5, and the third one corresponding to the estimated actual lead activity. B) Calibration curve recorded using tuned polarization in solutions from 10^{-7} to 10^{-9} mol dm^{-3} of Pb^{2+}, and current-off potentials recorded in a sample of 1.07 × 10^{-8} mol dm^{-3} Pb^{2+} with ISE polarized with the three respective currents (labelled in the figure), all with 10^{-3} mol dm^{-3} KNO_3 background.

To overcome this issue, a simple procedure of at least three measurements is required. Firstly, the electrode was polarized using a current density that was optimal to an arbitrarily chosen particular activity of lead, for example i_{opt} for pPb^{2+}= 7.2. The obtained potential was below the Nernstian value for pPb^{2+}= 7.2 which meant that the actual target analyte concentration was lower. In this case, another current density was applied but this time corresponding to much lower lead activity, for example i_{opt} for pPb^{2+}= 8.5. The potential obtained was on the other side of the calibration curve, thus the target analyte concentration was somewhere in between pPb^{2+}= 7.2 and pPb^{2+}= 8.5. None of the potentials belong to the calibration curve and when connected with a straight line they cross it. As shown elsewhere [136], the intersection point must correspond to the lead activity in the sample solution (1.07 × 10^{-8} mol dm^{-3} Pb^{2+}). To confirm this, an additional third run was performed with the current density optimal to the lead activity in the sample corresponding to the intersection point. Results show that the potential recorded for the electrode polarized by passing this optimal current was in good agreement with the potential at the intersection point, a result which confirms the correctness of the analysis. The determination of lead in each sample was performed three times. The delay between each measurement was approximately 24 hours. Only one calibration curve was prepared prior to the determinations, and thus corrections to the day-to-day deviations of the formal potential needed to be made. Therefore the deviation of the potential of the electrode in 10^{-7} mol dm^{-3} from the calibration curve and the potential of the electrode in sample solution were removed from the obtained data. In this way, the deviations of the current value of the formal potential from the calibration curve and that in the sample solution, as well as deviations caused by incomplete relaxation of the potential were eliminated. The average of three chronopotentiometric measurements indicated $pPb^{2+}= 7.97 \pm 0.08$ in the sample solution, while the ICP-MS analysis of the same samples showed pPb= 7.93. Both results are in good agreement and therefore suggest that solid-state membrane can be successfully applied in chronopotentiometric mode for the determination of lead in diluted samples.

8.9 Determination of Pb^{2+} by a solid-state (PbS/Ag_2S) membrane electrode in environmental sample by the tuned galvanostatic polarization method

Due to the limitations of the procedure based on time and concentration dependent conditioning of solid-contact Pb^{2+}-ISEs for lowering of the detection limit, the environmental sample was studied only by the more reliable method, the tuned galvanostatic polarization of solid-state PbS/Ag_2S membrane electrodes (***Paper VI***).

The sample was collected from the Finnish Archipelago, near to a previously industrially active terrain (silver mine). The pH, conductivity, and the redox potential of the native environmental sample were 5.04, 54.3 $\mu S\ cm^{-1}$, 330.3 mV, respectively. Additionally, a high quantity of particles (further classified as solid impurities) was observed in the environmental sample. However no further investigation of the nature and quantification of the suspension were performed. The determination was done in unbuffered pH, filtered and non-filtered environmental sample. Applying the tuned galvanostatic polarization method (chronopotentiometry) with a solid-state PbS/Ag_2S membrane created a unique possibility to measure Pb^{2+} pollution in an environmental sample. The analytical procedure used for Pb^{2+} determination is shown in Figures 27 A and B. Prior to the determination, a calibration curve was prepared in the range 10^{-6}-10^{-8} mol dm^{-3} $Pb(NO_3)_2$, with a constant background electrolyte (10^{-3} mol dm^{-3} KNO_3), by applying to the PbS/Ag_2S membrane current densities that were tuned for the specific lead activities (Figure 27 A, dotted lines). The procedure to obtain the calibration curve and further measurement was kept the same as in the case of the determination of Pb^{2+} in synthetic sample as described in chapter 8.8 of this thesis.

When analysing Pb^{2+} in environmental samples by using the tuned galvanostatic polarization approach there are two unknowns: the activity of the target analyte and the current density that is optimal for that particular ion activity. A procedure of at least three measurements in the environmental sample was applied. Firstly, the electrode was polarized by a current density that was optimal for arbitrarily chosen lead activity, for example i_{opt} for $pPb^{2+}= 6.5$. The potential value taken 0.2 s after the applied current was switched off was well below the calibration curve. The Pb^{2+} activity in the environmental sample was then lower than the assumed initial activity (pPb^{2+}= 6.5). Secondly, another current density corresponding to much lower activity of lead was applied, i_{opt} for pPb^{2+}= 7.7. The sampled value of potential was then well above the calibration curve for Pb^{2+}. This indicated that the target analyte concentration was in between pPb^{2+}= 6.5 and pPb^{2+}=7.7.

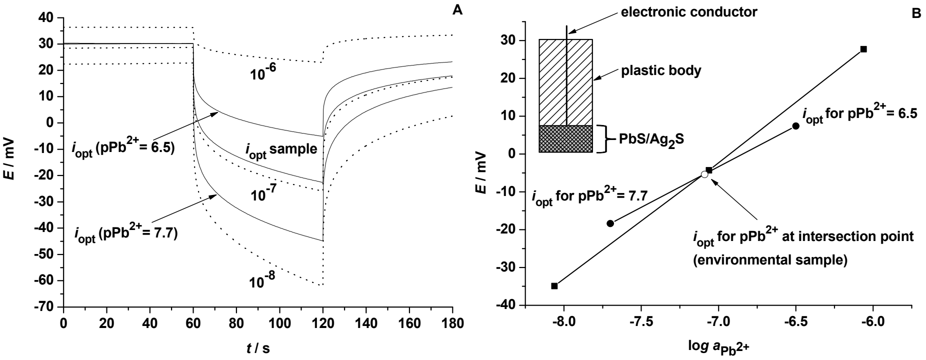

Figure 27. Analytical procedure of lead determination in the environmental sample: A) Three chronopotentiometric curves recorded with current densities tuned for 10^{-6}, 10^{-7}, and 10^{-8} mol dm^{-3} Pb^{2+} (dotted lines) used to plot Pb^{2+} calibration curve and three chronopotentiometric curves recorded with the two arbitrarily chosen current densities corresponding to pPb=6.5 and 7.7, and the third one corresponding to the estimated actual lead activity. B) Pb^{2+} calibration curve and current-off potentials recorded in the environmental sample by ISE polarized with the three respective currents (labelled in the figure), all with 10^{-3} mol dm^{-3} KNO_3 background. Insert: drawing of Pb^{2+} solid-state (PbS/Ag_2S) membrane electrode used in the tuned galvanostatic polarization method.

Relying on the principal that the polarization of the solid-state electrode is directly proportional to the applied current density, by applying mathematical procedures the Pb^{2+} activity may be defined [136]. When connecting the potential points obtained at different current densities for the environmental sample with a straight line, an intersection with the calibration curve was obtained. In this way the intersection point had to correspond to the lead activity in the environmental sample. As a confirmation of the correctness of the analysis, the last chronopotentiometric curve was recorded, but this time with the current density optimal to the lead activity in the environmental sample corresponding to the intersection point. Subsequently, the potential recorded for the electrode polarized by passing this optimal current was in good agreement with the potential at the intersection point. The determination of lead in the environmental sample was performed three times, and the Pb^{2+} concentration in a filtered environmental sample was found to be 17.2 ± 1.6 μg dm^{-3}. The same procedure of Pb^{2+} analysis was applied with the whole (non-filtered) sample. As a result of three consecutive measurements the Pb^{2+} concentration was found to be 16.1 ± 1.1 μg dm^{-3}.

The analysis performed by solid-state ISEs in chronopotentiometric mode was supported by inductively coupled plasma mass spectrometry (ICP-MS) measurements. The total concentrations of each element in the environmental sample are given in Table 6.

Table 6. Logarithmic values of total element concentrations, c_j (mol dm^{-3}) determined by ICP-MS analysis in the environmental sample.

Element (j) / $-\log c_j$		
V / 7.3	Zn / 5.3	Na / 4.2
Cr / 8.6	As / 7.5	Mg / 4.3
K / 4.4	Cd / 8.2	Al / 6.4
Fe / 5.9	Tl / 9.6	Ni / 7.6
Mn / 5.8	Pb / 7.1	Ag / 9.3
Ca / 3.7	Co / 8.2	Ba / 7.5
Li / 6.3	Cu / 6.7	U / 8.9

Owing to the presence of solid impurities, analysis using ICP-MS was only possible in the filtered sample. The total lead concentration in the environmental sample was 18.0 ± 0.4 μg dm^{-3}. A relatively small concentration of silver and high concentrations of potassium, calcium, zinc, and sodium were detected in comparison to the total lead concentration. Moreover, higher concentration of copper could have negatively influence the potentiometric measurements done with PbS/Ag_2S electrodes due to poor selectivity for Pb^{2+} over Cu^{2+}. Finally, the environmental sample contained significant concentrations of various species, so the major unfavourable effect came from the high ionic strength of the sample. To minimize this effect, the calibration curve for Pb^{2+} determination was intentionally prepared with constant background electrolyte pKNO_3= 3. No further studies of the free form of each component in the environonemental sample, except that of lead, were performed.

The concentration of lead(II) in the environmental sample was further investigated using differential pulse anodic stripping voltammetry (DPASV). The analysis of the environmental sample by DPASV is shown in Figures 28 A and B. After pre-treatment of the electrode system, the voltammograms were recorded for the environmental sample and subsequently after every standard addition (2 μg dm^{-3} Pb^{2+} per addition) with pre-concentration times (30 s, 32 s, 34 s, and 36 s). In total three additions were performed. Three voltammograms were recorded for the environmental sample after each standard addition for every pre-concentration time. A novel self-referencing background removal method was used to ensure high accuracy and precision of the obtained results. The procedure required different regression slopes (in our case for all pre-concentration times, R^2= 0.999) in order to remove the background in the most accurate manner, and therefore different accumulation times were used. After background current removal the current peak for the environmental sample and each Pb^{2+} addition was plotted against the concentration of the added standard. The concentration of Pb^{2+} (including five times dilution) in the environmental sample was determined to be 24.3 ± 0.5 μg dm^{-3}. However, when measuring in the non-filtered environmental sample high deviation of Pb^{2+} concentration was observed in comparison to the one obtained from the filtered sample.

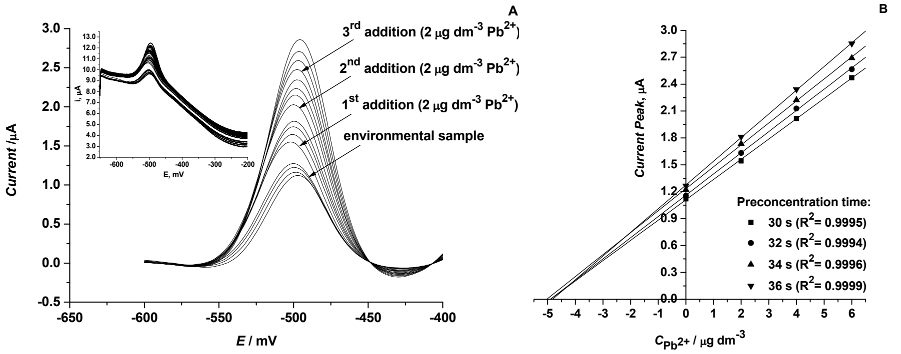

Figure 28. Analytical procedure of lead determination in the environmental sample by differential pulse anodic stripping voltammetry: A) Averaged current peaks (from three repetitions) obtained after background removal form the sample and three consecutive Pb^{2+} standard additions (each 2 μg dm^{-3} Pb^{2+}), each recorded at four (30 s, 32 s, 34 s, and 36 s) pre-concentration times. Insert: Recorded voltammograms before background removal. B) Standard addition method for determination of lead(II) with regression fit from Pb^{2+} standard additions to the environmental sample (for each R^2= 0.999) at various pre-concentration times.

A comparison of the results obtained by TGP, ICP-MS, and DPASV is presented in Table 7. For the filtered environmental sample, the concentration of Pb^{2+} recorded was similar for the tuned galvanostatic polarization method and ICP-MS measurements. Higher concentrations were obtained using DPASV. The uncertainties of the ICP-MS and DPASV measurements were similar and relatively small. The chronopotentiometric measurement was characterized by slightly higher uncertainties; however, the possibility of measurement with similar accuracy in the non-filtered and filtered environmental samples for solid-state PbS/Ag_2S electrodes is truly advantageous. The other methods were not suitable for non-filtered environmental sample. In case of the ICP-MS instrument, particles bigger than 0.45 μm in diameter had to be removed to prevent tube-clotting. In case of the DPASV measurements in the non-filtered samples showed approximately one order of magnitude higher Pb^{2+} concentration compared to the filtered one.

Table 7. Comparison of lead concentrations obtained by various techniques.

Technique	Sample	Concentration of Pb^{2+} in the environmental sample (n= 3), μg dm^{-3}
Tuned galvanostatic polarization (solid-state Pb^{2+}-ISEs)	filtered	17.2 ± 1.6
	non-filtered	16.1 ± 1.1
Inductively coupled plasma mass spectrometry (ICP-MS) (total Pb concent.)	filtered	18.0 ± 0.4
	non-filtered	unattainable*
Differential pulse anodic stripping voltammetry (DPASV)	filtered	24.3 ± 0.5
	non-filtered	unreliable**

* the tube-clogging of the ICP-MS instrument

** one order of magnitude higher Pb^{2+} concentration than for filtered sample

Despite the relatively poor selectivity of solid-state electrodes, the determination of lead (II) was possible due to the composition of the sample. A significant concentration of copper was recorded. However, it was complexed/adsorbed by solid impurities (most probably humic/fulvic substances) present in the sample; e.g. at pH 5 (as in the environmental sample) the presence of copper, calcium, magnesium, zinc, and nickel effectively compete for complex formation with fulvic acid (FA), and significantly decrease the ability to form Pb^{2+}-FA complexes [204]. To support this, a simple but effective measurement was performed. The environmental sample was acidified with the addition of 5 mol dm^{-3} HCl to the pH 1.75, and stirred for 2 hours to release accumulated lead from complexes and/or solid matter. Subsequently, by the addition of 1 mol dm^{-3} NaOH the pH was brought to 4 and analysis using the tuned galvanostatic polarization method was performed with the PbS/Ag_2S membrane. The obtained result showed an increase in lead concentration to 84.4 μg dm^{-3}, which indicates the partial release of bound lead into the solution.

9. Conclusions and closing remarks

Throughout my study a series of different types of Pb^{2+}-selective electrodes have been developed and applied as sensors for the determination of lead in various samples. The thesis covers the implementation of various matrix materials, such as PVC, polycarylate co-polymer and polycrystalline materials, the application of different electrode designs as well as the development and implementation of novel methods of measurement, for example the concentration and time dependent conditioning of solid-contact Pb^{2+}-ISEs with recovery of *LDL* at lowest analyte concentrations; kinetic calibration based on adsorption of the analyte on the surface of the electrode after the same pre-treatment for solid-state PbS/Ag_2S membrane electrodes; and the tuned galvanostatic polarization of PbS/Ag_2S membrane electrodes.

The polyacrylate co-polymer matrix was applied in conventional types of Pb^{2+}-ISE to stop transmembrane ion fluxes from the inner reference solution. Although the fluxes were significantly diminished, the lower detection limit was not improved in comparison to PVC-based Pb^{2+}-ISE. This aspect, however, was not investigated enough as the measurement and the pre-treatment of the electrodes was not optimized for lowering the detection limit, for example by exposing electrodes to relatively concentrated lead(II) solutions.

Owning to the limitation of the thermopolymerization of the polyacrylate matrix and the lack of a highly selective ionophore that could be used in that matrix, further studies concentrated on PVC-based membranes in all-solid state configuration. Polybenzopyrene doped with eriochrome black T was developed and used as Pb^{2+} sensitive film. It was possible owning to the complexation properties of eriochrome black T with lead(II). This system however was lacking selectivity toward Pb^{2+} over other ions to be directly used in lowering the detection limit. As it did not exhibit the unfavourable “memory effect”, the conducting film was further applied as solid contact material for polybenzopyrene(EbT) electrodes coated with PVC-based membranes containing the lead IV ionophore.

Taking advantage of the prior knowledge that the low detection limit is concentration and time dependent, the lowering of the detection limit of solid-contact Pb^{2+}-ISEs was possible by applying a strict protocol of pre-treatment, conditioning, and measurement procedure. The concentration and time dependent conditioning of solid-contact Pb^{2+}-ISEs with recovery of the detection limit at the lowest analyte concentrations was developed and used to reach Nernstian response close to nanomolar Pb^{2+} concentrations. Recovery of the lower detection limit at low analyte concentration was obtained by conditioning of the electrode in Na_2EDTA solution. By introducing Na^+ to the ISM and simultaneously reversing Pb^{2+} flux from the membrane, complexing adsorbed (at the ISM) and extracted (from the ISM) lead, together with complexing any other impurities from the membrane surface the recovery of the response at extremely low concentrations, was achieved. The selectivity toward Pb^{2+} allowed this sensor to be used in the determination of Pb^{2+} in synthetic samples.

Furthermore, the idea of implementing solid-state PbS/Ag_2S membrane sensors in lowering of the detection limit was investigated. Although the first works concerning *LDL* were devoted to solid-state sensors in the 1970's they were somehow forgotten following the discovery of plastic membranes. By applying current knowledge on lowering the detection limit, and taking advantage of what was previously achieved with solid-state ISEs, novel approaches to lowering the detection limit were explored. It was found that by optimizing the conditions in the solutions, for example, minimizing side reactions and parasitic processes, and by the use of a procedure of cleaning the membrane and introducing optimized readout times (kinetic method) - it was possible to extend the linear measurement range for the solid-state PbS/Ag_2S membrane lead(II)-ISEs in unbuffered solutions down to $10^{-8.0}$ mol dm^{-3} Pb^{2+}.

Another method of lowering the detection limit of the solid-state PbS/Ag_2S membrane electrodes was obtained by applying tuned galvanostatic polarization. In this method, the current enables the membrane to work in less oxidizing conditions and the detection limit can be drastically improved. Good sensitivity with a Nernstian slope down to 10^{-9} mol dm^{-3} was achieved. The advantages such as short time of analysis, repeatability of the results, ease of the operations, together with the robustness of solid-state membranes, provide excellent opportunities to measure reliably in the nanomolar concentration range. From a practical point of view, and in comparison to heavily advertised possibilities obtained with plastic-based Pb^{2+}-ISEs, this is an attractive opportunity. Additionally, the use of a solid-state type ion-selective electrode eliminates the problem with uncontrolled transmembrane ion fluxes, which solvent polymeric membranes suffer from, and thus the analysis for solid-state membranes is generally simpler. The tuned galvanostatic polarization method with solid-state electrodes was used for the determination of Pb^{2+} in synthetic and environmental samples.

By applying a well-established analytical protocol, lead activity was correctly determined in synthetic samples by solid-contact and solid-state Pb^{2+}-ISEs. The determination was validated by ICP-MS measurements. For the concentration and time dependent conditioning of solid-contact Pb^{2+}-ISEs with recovery of the detection limit at lowest analyte concentrations, the determination of lead was performed by implementing direct potentiometry and the single standard addition method. Since in this method the analysis is performed at non-equilibrium conditions the formal potential of electrodes shifts with every measurement and more reliable readouts were obtained when applying the single standard addition method. Owning to the limitations, the determination of lead in the environmental sample was not further investigated using this method.

On the other hand, successful implementation of the tuned galvanostatic polarization method with PbS/Ag_2S membrane electrodes led to the direct determination of Pb^{2+} in synthetic sample. Further, the simple procedure for measurement created the possibility of applying solid-state electrodes in the measurements of lead(II) in an environmental sample. Although the sample matrix was undefined, the tuned galvanostatic polarization method was successfully applied for the determination of Pb^{2+} in laboratory scale analysis. The potentiometric determination was favourably compared with inductively coupled plasma mass spectrometry and differential pulse anodic stripping voltammetry. I believe that the tuned galvanostatic polarization method may possibly be used to measure ionized lead on site (at environmental conditions with maintenance limited to minimum) when taking into account its miniaturization, automatization of calibration and measurement procedures, optimization of surface renewal, and powering of portable electrode systems.

Although uncertainty of chronopotentiometric measurement was the highest (yet acceptable in terms of reliable Pb^{2+} analysis) among all three methods, the true advantage of this method is in the possibility of measurement in the whole (non-filtered) environmental sample despite the presence of solid impurities that other applied methods were suffering from. Thus the tuned galvanostatic polarization method was successfully applied in the determination of Pb^{2+} in environmental sample. However, this was realized on laboratory scale and limitations of maintenance and equipment create concerns about applying the method and electrodes in environmental conditions. More measurements with environmental samples are needed to truly validate the use of the method. A simpler measuring unit with data acquisition and powering is also required if considering applying this method in autonomous field deployable system.

10 References

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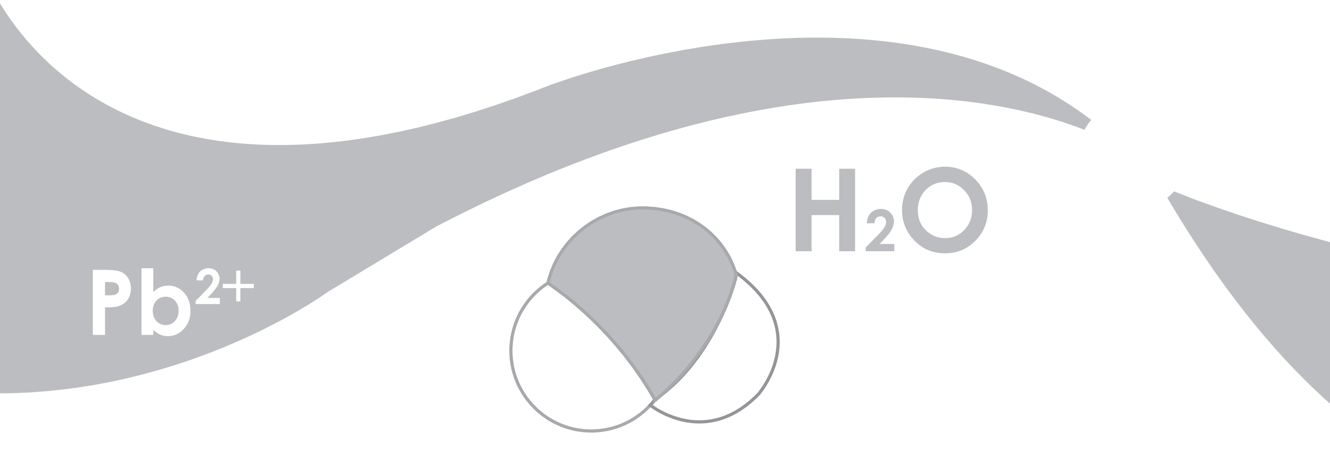

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