Substantiation of the Proposal of Credit Mobility BRAZIL – Prof. Barek

1. **Existing long term cooperation** with prof. J C. Moreira and prof. Célia Regina Sousa da Silva, Federal University of Rio de Janeiro (UFRJ) and CESTEH in electroanalytical chemistry of genotoxic compounds and tumor biomarkers. This cooperation, which is based on attached agreement, resulted in more 30 joint papers the list of which is attached at the end of this substantiation. In the last 20 years more than 10 staff members from UNESCO Laboratory of environmental electrochemistry visited UFRJ and CESTEH; the total time of visits exceeded 3 years. Analogously, more than 5 researchers from Rio visited UNESCO Laboratory of environmental electrochemistry at Charles University; the total time of their visits exceed 1 year. Selected joint papers are attached at the end of this document.

2. **Interest in prolongation and broadening of existing cooperation** is documented by the fact that at present two PhD students from our laboratory (Mgr. Jan Mika, Mgr. Jaroslava Zavázková) work at UFRJ on 5 months research stay on the development of electroanalytical methods for monitoring of tumor biomarkers and one research worker from UFRJ (Dr. Rene Pfeifer) works on the same topic in the frame of his one year stay in our laboratory.

3. **The agreement on joint PhD study (cotutelle)** in the field of electroanalytical chemistry is prepared and approved by both sides.

4. **Considerable experience of both sides in the field of ERASMUS projects implementation** is obvious from the above given facts and from the fact that UNESCO Laboratory of environmental electrochemistry is among the most active units at Faculty of Science of Charles University in the field of sending out and accepting of students in ERASMUS exchange programs.

5. **High quality of partner university and responsible person on Brazilian side** - Prof. Prof. Célia Regina Sousa da Silva from UFRJ is among top Brazilian experts in the field of electroanalytical methods.

**List of joint paper with Brazilian coworkers**

Selected joint papers with Brazilian coworkers – (only first page because of limited space)
Modern Electrochemical Methods for Monitoring of Chemical Carcinogens

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Abstract: This contribution is based on our presentation at the 1st International Symposium on Sensor Science, Paris, 16-20 June 2003. It presents recent results regarding the electrochemical determination of subnanomolar and nanomolar concentrations of various carcinogenic substances (nitroated polycyclic aromatic hydrocarbons, heterocyclic compounds, azo compounds, aromatic amino compounds, etc.) using both traditional (classical dropping mercury electrode, static mercury drop electrode, hanging mercury drop electrode) and non-traditional types of electrodes (solid amalgam electrodes, carbon paste electrodes, platinum tubular electrodes).

Keywords: mercury electrodes, solid amalgam electrodes, carbon paste electrodes, carcinogens.
The use of silver solid amalgam electrode for voltammetric and amperometric determination of nitroquinolines

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ABSTRACT

Solid amalgam electrodes represent a suitable alternative to mercury electrodes due to their similar electrochemical properties and non-toxicity of the amalgam material. Nitro derivatives of quinoline have been proven to be genotoxic, thus their presence in environmental samples is a legitimate cause for concern. In this contribution, meniscus modified silver solid amalgam electrode (m-AGSE) was employed for the batch voltammetric determination and amperometric determination in connection with flow injection analysis of 5-nitroquinoline and 6-nitroquinoline (5-NQ, 6-NQ). Their electrochemical behavior was characterized by cyclic voltammetry. For their determination direct current voltammetry and differential pulse voltammetry were used. Linear calibration curves in the concentration range of $2 \times 10^{-7}$ to $1 \times 10^{-6}$ mol L$^{-1}$ were obtained. These results are comparable to those obtained for polarographic determination of the same substances using mercury electrodes. Further, the meniscus modified silver solid amalgam electrode was employed in amperometric detection cell in "wall jet" arrangement for determination of 5-NQ by flow injection analysis. Under optimized conditions (run buffer 0.05 mol L$^{-1}$ borate buffer, pH 9.0; flow-rate 4 ml min$^{-1}$; detection potential -1.6 V; injection volume 0.1 ml), the limit of quantification of $4 \times 10^{-4}$ mol L$^{-1}$ was achieved. The repeatability of the detector response is satisfactory with a relative standard deviation of $2.1\%$ for $5 \times 10^{-6}$ mol L$^{-1}$ 5-NQ. Practical applicability of the method was verified for the determination of micromolar concentrations of 5-NQ in leaching and river water samples.

1. Introduction

Solid amalgam electrodes (SAE), introduced in electrochemistry in the year 2000 by independent research groups from Prague (Czech Republic) and Trondheim Norway, represent electrochemically most similar alternative to mercury electrodes. Besides the similar properties like wide cathodic potential window and relatively high sensitivity, SAE add several additional benefits to mercury electrodes. Generally, respect the non-toxicity of amalgam materials reliably proven during decades of their usage in neurology. This makes SAE comparable with the concept of "green analytical chemistry" and suitable for their broad expansion. Among other advantages of amalgam electrodes benogs mechanical robustness that allows their application in flow liquid systems (e.g., flow injection analysis (FLA) or high-performance liquid chromatography (HPLC)) as working electrodes of electrochemical detectors.

While the Trondheim research group developed solid amalgam electrodes based on silver dental amalgam [2] and its research is directed to heavy metals analysis [3–5], the electrodes prepared by the Prague group feature a variety of metals used for amalgam preparation (e.g., silver, copper, gold and thallium). They can be used either as mercury-free electrodes after polishing of solid amalgam disc (p-AGSSE) or after modification of their surfaces by mercury film (MF-MSAE) or mercury meniscus (m-MSAE). Among all the metals used, silver seems to perform best of all the MSSE for analytes missing specific interactions (e.g., complexation with metal cations) with metals of the amalgam. In the case of m-MSSE or MF-AGSSE, the liquid mercury film or meniscus gives to the electrode almost ideally smooth and isotropic surface and electrochemical properties comparable with mercury electrodes. If there is no significant interaction of analyte with silver component of AgSSE, the analytical performance in many cases approaches to mercury electrodes [67]. It was proved by a variety of electroanalytical applications, including the voltammetric determination of heavy metals cations ([Cu$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Fe$^{3+}$, Ni$^{2+}$, Ti$^{4+}$, In$^{3+}$, Cr$^{3+}$] and some inorganics anions (NO$_3^-$, I$^-$, Br$^-$, SCN$^-$)) [6,8–10]. Moreover, m-AGSAE and m-CoSSE were employed for the...
Voltammetric Determination of N-Nitroso Antineoplastic Drugs at Mercury and Amalgam Electrodes

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Abstract: In this contribution, the possibilities and limitations of hanging mercury drop electrode (HMDE) and mercury meniscus modified silver solid amalgam electrode (m-AgSAE) as electroanalytical sensors for voltammetric determination of carmustine and streptozotocin are shown. Both these analytes contain reducible N-nitroso group and are classified as antineoplastic chemotherapy drugs. The electrochemical behaviour of carmustine and streptozotocin was studied by DC voltammetry and differential pulse voltammetry, the reduction of N-nitroso group at m-AgSAE proceeds at substantially more negative potentials than at HMDE in the whole investigated pH range (2.0-10.0). Both electrodes offer satisfactory repeatability of current response (relative standard deviation < 3 %), the repeatability at solid m-AgSAE was assured by electrochemical pretreatment of the electrode surface. Achieved limits of determination lye in the 10⁻⁷ mol L⁻¹ concentration range, slightly lower values were obtained for HMDE than for m-AgSAE.

Keywords: Carmustine, streptozotocin; DC voltammetry, differential pulse voltammetry; hanging mercury drop electrode; amalgam electrode.
Non-Traditional Electrode Materials for Detection of Biomarkers

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\textsuperscript{2} National School of Public Health, FIOCRUZ, Rua Leopoldo Bulhões, 1480 - Manginhos, Rio de Janeiro, Brazil.
\textsuperscript{3} University of California San Diego (UCSD), La Jolla, Department of Nanoengineering, 9500 Gilman Drive 0448, CA 92093-0448, USA.

\textbf{Abstract}: In this paper, new electrochemical methods suitable for detection of various types of biomarkers (biomarkers of esposition, tumor biomarkers, and biomarkers of medical treatment) are briefly reviewed. Attention is paid to the use of non-traditional electrode materials (various forms of amalgam electrodes, boron dopel diamond film electrodes, carbon paste and carbon film electrodes, etc.) for voltammetric (batch analysis) and amperometric (flowing systems) detection of above mentioned biomarkers.

\textbf{Keywords}: Amalgam electrodes; Carbon paste electrodes; Boron doped diamond film electrodes; Differential pulse voltammetry; Amperometry; Biologically active organic compounds; Biomarkers; Tumor markers; Markers of Medical Treatment.

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\textbf{Introduction}

There is an ever increasing demand for analytical methods applicable for monitoring of various biomarkers (BM) in human organism. Electroanalytical methods, namely voltammetry and amperometry, allow large scale screening of selected electrochemically active BM because they are inexpensive, fast, simple, sufficiently sensitive and selective and
Voltammetric and Amperometric Determination of Biologically Active Organic Compounds Using Various Types of Silver Amalgam Electrodes

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\textsuperscript{3} University of California San Diego (UCSD), La Jolla, Department of Nanoengineering, 9500 Gilman Drive 0448, CA 92093-0448, USA.

Abstract: In this paper, possibilities of various types of silver amalgam electrodes for determination of micromolar and submicromolar concentrations of various electrochemically reducible biologically active organic compounds are reviewed. Attention is paid to the use of polished and mercury meniscus modified silver solid amalgam electrode, silver amalgam paste electrodes both with and without pasting liquids, single crystal silver amalgam electrodes, composite silver amalgam electrodes, and porous silver amalgam electrodes. Main focus is on voltammetric application of above mentioned electrodes. However, their application in flowing systems (high performance liquid chromatography and flow injection analysis with electrochemical detection) is briefly discussed as well. The compatibility of various types of silver amalgam electrodes with preliminary separation based on solid phase extraction is demonstrated on determination of nanomolar concentrations of environmentally important compounds in model samples of drinking and river waters.

Keywords: Silver solid amalgam electrodes; Silver amalgam paste electrodes; Single crystal silver amalgam electrodes; Composite silver amalgam electrodes; Porous silver amalgam electrodes; Differential pulse voltammetry; Amperometry; Biologically active compounds.

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The use of silver solid amalgam electrode for voltammetric and amperometric determination of nitroquinolines

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In this contribution, menisco modified silver solid amalgam electrode (m-AgSAE) was employed for the first voltametric determination and amperometric determination in connection with flow injections analysis of 5-nitrosoquinoline and 6-nitrosoquinoline (5-NQ, 6-NQ). Their electrochemical behavior was characterized by cyclic voltammetry, for their determination direct current voltammetry and differential pulse voltammetry were used. Linear calibration curves in the concentration range of 2 x 10^-7 to 1 x 10^-4 mol L^-1 were obtained. These results are comparable with results obtained for polarographic determination of the same substances using mercury electrode. Further, the menisco modified silver solid amalgam electrodes were employed in amperometric detection cell in "wall jet" arrangement for determination of 5-NQ in flow injection analysis. Under optimized conditions (run buffer 0.05 mol L^-1 borate buffer, pH 9.0; flow rate 4.0 ml min^-1 detection potential -1.63 V, injection volume 1.0 ml), the limit of quantification of -4 x 10^-7 mol L^-1 was achieved. The repeatability of the detector response is satisfactory (relative standard deviation 2.15% for 5-NQ at 1 x 10^-5 mol L^-1). Practical applicability of the method was verified for the determination of micromolar concentrations of 5-NQ in drinking and river water model samples.

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1. Introduction

Solid amalgam electrodes (SAE), introduced in electrochemistry in the year 2000 by independent research groups from Prague (Czech Republic) [1] and Trondheim (Norway) [2], represent electrochemically most similar alternative to mercury electrodes. Beside the similar properties like wide cathodic potential window and relatively high sensitivity, SAE add several additional benefits to mercury electrodes. Generally respected is the non-toxicity of amalgam materials reliably proven during decades of their usage in ortodonty. This makes SAE compatible with the concept of "green analytical chemistry" and suitable for their broad expansion. Among other advantages of amalgam electrodes belong: mechanical robustness that allows their application in flow liquid systems (e.g. flow injection analysis (FIA) or high-performance liquid chromatography (HPLC)) as working electrodes of electrochemical detectors.

While the Trondheim research group developed solid amalgam electrodes based on silver dental amalgams [2] and its research is directed to heavy metals analysis [3-5], the electrodes prepared by the Prague group feature variety of metals used for amalgam preparation (e.g., silver, copper, gold and thallium). They can be used either as mercury-free electrodes after polishing of solid amalgam disc (p-MeSAE) or after modification of their surfaces by mercury film (MF-MeSAE) or mercury m menisco (m-MeSAE). Among all the metals used, silver seems to perform best of all MeSAE for analyses missing specific interaction (e.g., complexation with metal cations) with metals of the amalgam. In the case of m-AgSAE or MF-AgSAE, the liquid mercury film on meniscus gives to the electrode almost ideal smooth and isotropic surface and electrochemical properties comparable with mercury electrodes. If there is no significant interaction of analytes with silver component of AgSAE, the analytical performance in many cases approaches to mercury electrodes [6,7]. It was proved by a variety of electroanalytical applications, including the voltammetric determination of heavy metals cations (Cu²⁺, Pb²⁺, Cd²⁺, Zn²⁺, Fe⁴⁺, Ni²⁺, Tl⁺, In³⁺, Cr⁷⁺) and some inorganic anions (NO₃⁻, IO₃⁻, I⁻, Br⁻, SCN⁻) [6,8-10]. Moreover, m-AgSAE and m-CuSAE were employed for the
AGREEMENT OF COOPERATION 
BETWEEN 
THE OSWALDO CRUZ FOUNDATION (FIOCRUZ) 
AND 
FACULTY OF SCIENCE, CHARLES UNIVERSITY, 
PRAGUE 

The Oswaldo Cruz Foundation (FIOCRUZ), Federal Public Administration Unit, linked to the Ministry of Health of Brazil, at Av. Brasil, 4365 - Manguinhos, Rio de Janeiro - RJ, Brasil, represented by its President Dr. ELOI DE SOUZA GARCIA, and the Faculty of Science, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic, represented by its Dean Prof. KAREL STULÍK, DSc, in perfect union with their interests, agree to collaborate in fields of research to be agreed on. The form of cooperation will be such as:

* Joint research activities and publications;
* Exchange of invitations to scholars for lectures, talks and sharing of experience;
* Exchange of invitations to scholars to participate in conferences, colloquia and symposia;
* Exchange of information in fields of interest to both institutions;
* Exchange of faculty members and students for study and research.

1. The above mentioned activities shall be financed according to the availability of funds.

2. All travel and living expenses shall be carried by the respective home institution.

3. Both parties agree to endeavor to secure the funds necessary for this cooperation, such as foundations, scholarship organisations and other donors (institutions or persons).