Functionalized track-etched membranes for electrochemical sensing of toxic metals in water

1. Introduction

Heavy metal ions, including Hg^{2+}, Pb^{2+}, Cd^{2+}, and UO_2^{2+}, are persistent, non-biodegradable contaminants that accumulate in aquatic ecosystems and pose severe toxicological risks at trace (sub-ppb, or µg/L) concentrations. Reliable monitoring of these species in natural and industrial waters is therefore required by international and national environmental legislation and represents an ongoing analytical challenge.

Conventional reference techniques such as ICP-MS and AAS offer adequate sensitivity but require centralized laboratory infrastructure, sample preparation campaigns, and skilled operators, making them unsuitable for rapid field deployment. Stripping voltammetry provides a compelling alternative: it combines sub-ppb detection limits with instrumental simplicity and straightforward miniaturization. Sensitivity is governed primarily by the preconcentration efficiency of the working electrode, so materials with high electroactive surface area and chemically selective metal-binding sites are central to sensor performance.

Track-etched membranes (TEMs) fabricated from swift heavy ion (SHI)-irradiated poly(vinylidene fluoride) (PVDF) offer a well-suited base polymer for this purpose. Chemical etching of latent ion tracks in concentrated alkaline $KOH/KMnO_4$ solution yields geometrically uniform cylindrical nanochannels whose diameter is controlled by etching conditions [1, 2]. Radiation-induced graft polymerization (RIGP) exploits long-lived radicals trapped along the pore walls to grow functional polymer chains, for instance poly(4-vinylpyridine) (P4VP) or poly(1-vinylimidazole) (PVIm), directly inside the nanochannels without external initiator [3]. Magnetron sputtering of a thin gold film onto both faces of the functionalized membrane converts it into an electrode with a large, chemically selective internal surface. This architecture has been shown to enable sub-ppb detection of Pb^{2+} by square-wave anodic stripping voltammetry (SW-ASV) [4, 5], and analogous systems targeting Hg^{2+} and other heavy metals are under active development at JINR's Flerov Laboratory of Nuclear Reactions (FLNR) [2, 6].

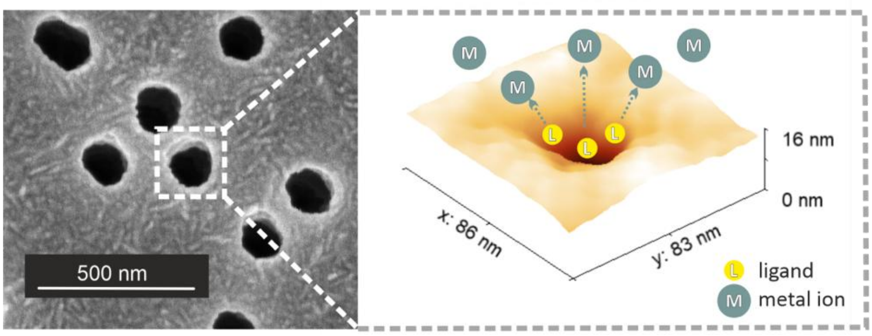

Figure 1 – Nanopore-confined functionalization of PVDF track-etched membrane for efficient preconcentration of dissolved toxic metal ions

2. Student Learning Outcomes

During this 3-week practice, participants will gain experience in a multidisciplinary research environment combining nuclear physics methods, polymer chemistry, and analytical electrochemistry. The student will:

– Understand the fundamentals of swift heavy ion interaction with polymers and the principles of track-etching technology;
– Learn laboratory protocols for radiation-induced graft polymerization of functional monomers within nanoscale confinement;
– Acquire practical skills in magnetron sputtering of metal contacts and the assembly of electrochemical sensors;
– Practice stripping voltammetry for quantitative analysis of heavy metals;
– Analyze experimental data and understand the correlation between grafting yield, pore structure, and sensor sensitivity.

3. Description of Work on the Project

3.1. Experimental Setup

The work will be carried out using the facilities of the FLNR that include: Schlenk line for degassing reaction solutions, magnetron sputtering system for gold deposition, potentiostat-galvanostat for conducting electrochemical measurements. The developed at FLNR set-up for on-site toxic metal analysis is demonstrated in Figure 2.

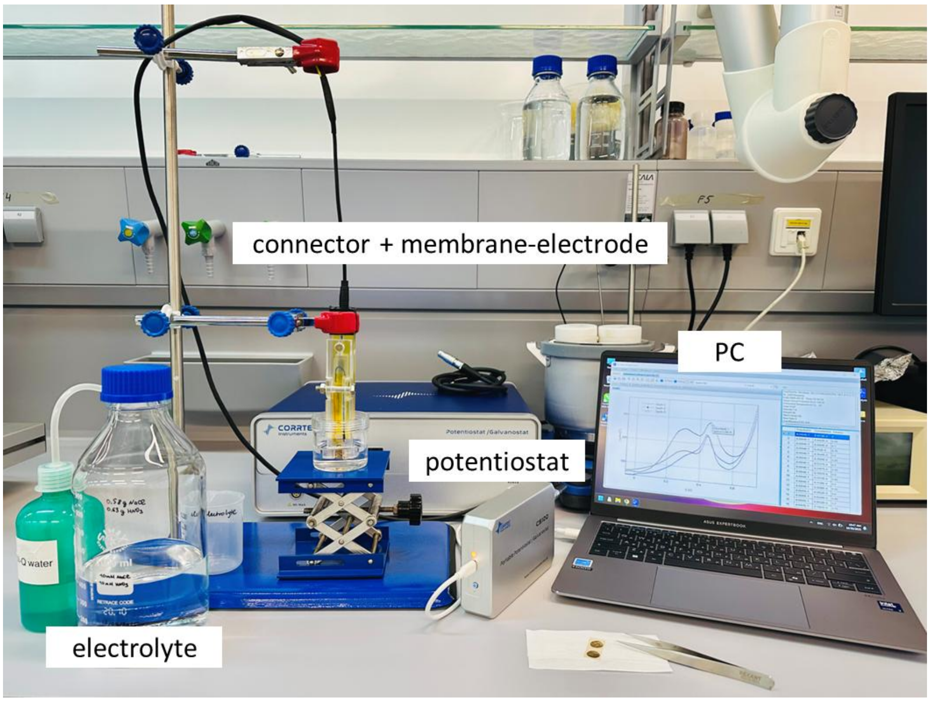

Figure 2 – Experimental set-up for electrochemical analysis using functionalized membrane-electrodes

3.2. Student Tasks

The student will follow a structured workflow over the three weeks:

Week 1: Membrane Fabrication and Functionalization

Etching: The student will be provided with pre-irradiated PVDF foils (Xe ions, 1.2-3.8 MeV/nucleon, ion fluence of 10^9 ions/cm^2). Under supervision, they will perform chemical etching in a 10M KOH/0.1M $KMnO_4$ solution at 65°C to reveal cylindrical nanopores (diameter ~50 nm).

Grafting: The etched membranes will be placed in a Schlenk tube with a functional monomer solution (for instance, 4-vinylpyridine or 1-vinylimidazole). After argon purging to remove oxygen, the reaction will proceed at 60°C for a specific duration to initiate polymerization from residual radicals. The student will calculate the gravimetric grafting yield (GY, wt.%).

Electrode deposition: The student will use a magnetron sputtering machine to deposit a thin conductive layer of gold (~50 nm) onto both sides of the functionalized membrane through a mask, defining the working electrode area. This will also include a brief training on Scanning Electron Microscopy (SEM) to verify pore openness and gold layer uniformity.

Week 2: Electrochemical Analysis

Calibration curve: The membrane-electrodes will be immersed in model aqueous solutions spiked with heavy metal ions (*e.g.*, Hg^{2+}) under stirring for passive adsorption. The student will connect the sensor to a potentiostat (Palmsens or Corrtest) and perform Square-Wave Anodic Stripping Voltammetry (SW-ASV) using optimized parameters such as deposition potential, deposition time, and frequency to register the stripping peak current. This data will serve for plotting a calibration curve (peak current *vs.* metal ion concentration) to evaluate sensor sensitivity and detection limit.

Week 3: Matrix effects

Interference studies: The membrane-electrode operating ability will be tested in the presence of other interfering metal ions, salts and pH.

3.3. Presentation of Results

At the end of the practice, the student will submit an electronic report summarizing the work. The report should include:

- A brief introduction to track-etched membranes and radiation grafting;
- Description of experimental conditions (etching time, grafting solution, voltammetry parameters);
- SEM images of the membrane surface;
- Voltammograms and the resulting calibration curves;
- Calculation of the Limit of Detection (LOD) for the target metal ion.

4. Requirements for Student Background

Level: Final-year Bachelor students or 1st / 2nd-year Master students.

Field of Study: Physical Chemistry, Materials Science, or Nanotechnology. Prior experience with electrochemical methods is an advantage but not mandatory.

5. Recommended Literature

1. Apel, P. Y. (2019). Fabrication of functional micro- and nanoporous materials from polymers modified by swift heavy ions. *Radiation Physics and Chemistry*, 159, 25-24. https://doi.org/10.1016/j.radphyschem.2019.01.009

2. Kryukova-Seliverstova, A.V., Orelovich, O.L. et al. (2025). Radiation Grafting of PVDF Track-Etched Membranes: A Study for Nanoscale Pore Functionalization. *Eurasian Journal of Chemistry*. https://doi.org/10.31489/2959-0663/3-25-9

3. Betz, N. (1995). Ion track grafting. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 105(1-4), 55-62. https://doi.org/10.1016/0168-583X(95)00911-6

4. Cuscito, O., Clochard, M. C., Esnouf, S., Betz, N., & Lairez, D. (2007). Nanoporous β-PVDF membranes with selectively functionalized pores. *Nuclear Instruments and Methods in Physics Research Section B*, 265(1), 309–313. https://doi.org/10.1016/j.nimb.2007.08.089

5. Bessbousse, H., Nandhakumar, I., Decker, M., Barsbay, M., Cuscito, O., Lairez, D., ... & Wade, T. L. (2011). Functionalized nanoporous track-etched β-PVDF membrane electrodes for lead (II) determination by square wave anodic stripping voltammetry. *Analytical Methods*, 3(6), 1351–1359. https://doi.org/10.1039/C1AY05038A

6. Pinaeva, U., Dietz, T. C., et al. (2019). Bis[2-(methacryloyloxy)ethyl] phosphate radiografted into track-etched PVDF for uranium (VI) determination by means of cathodic stripping voltammetry. *Reactive and Functional Polymers*, 142, 77-86. https://doi.org/10.1016/j.reactfunctpolym.2019.06.006

6. Number of Project Participants

1-2 students can work on this project simultaneously. The work can be performed individually or in a small team depending on the number of assigned students (for instance, one student focuses on grafting while the other focuses on electrochemistry, sharing characterization tasks).

7. Project Supervisor from JINR

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Research Interests: Radiation chemistry of polymers, swift heavy ion tracks, functional nanoporous membranes, radiation-induced graft polymerization