Self-plasticized poly(vinyl chloride) (PVC) derivatives for ion-selective electrode matrices

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Poly(vinyl chloride) (PVC) is a highly versatile material used across industries such as healthcare, electronics, construction, and consumer products. To increase its flexibility, PVC is combined with plasticizers, which make the polymer softer and malleable by lowering its glass transition temperature. This PVC-plasticizer blend is also commonly used in ion-selective electrodes (ISEs), where it helps create membranes that are softer, more flexible and offer a more favourable diffusion coefficient for improved performance. However, a significant issue with these PVC matrices is the gradual leaching of membrane components, such as the plasticizer, ionophores and ion-exchangers. This loss leads to a decline in selectivity, sensitivity, overall lifetime[1] and may also raise concerns about cytotoxicity, particularly for sensors intended for in vivo use[2].

Various approaches have been explored to prevent the leaching of membrane components. One common method involves adjusting the ratios of methacrylate-type or methacrylic-acrylic-type copolymer monomers in the matrix, thus avoiding the use of plasticizers[3]. For PVC-based materials, the simple, high yielding, click chemistry has been a key technique for immobilizing ionophores directly onto PVC chains through azide modifications[4]. Additionally, efforts have been made to covalently link plasticizers directly to PVC to address issues related to viscosity, flexibility, and thermal stability of the polymer. For example, Navarro et al. grafted a thiol-modified DEHP plasticizer onto the PVC backbone, creating an internally plasticized polymer[5].

We describe here the synthesis of a new class of self-plasticized poly(vinyl chloride) (PVC) derivatives for ion selective electrodes inspired by the synthetic works of Braslau et al.[6]. A tethered DEHP plasticizer -like analogue was grafted onto an azide-modified PVC backbone by tapping into click chemistry, using the simple, high-yielding, copper-catalyzed azide-alkyne cycloaddition reaction. The resultant polymer creates a flexible and stretchable film, obviating the need for an additional plasticizer to aid the dissolution of sensing components and ion diffusion through the ion-selective membrane, potentially resulting in leak-free and operational sensors.

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The chemistry behind 19th century Swiss blue stamps

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Identifying the components used in the manufacture of artworks is essential for understanding their history, as well as the cultural, technological and economic aspects of societies. The identification of pigments in postage stamps is a case in point. The mid-19th century saw the start of a revolutionary practice in the postal sector, the introduction of the first postage stamp, the iconic Penny Black in the United Kingdom in May 1840. In Switzerland, it was not until 1843 that the cantons produced their first stamps, and 1850 for federal issues [1]. Nowadays, they are an integral part of the world's cultural heritage due to their historical and social significance and constitute a unique form of art, and are, in some cases, very rare and precious. Despite their historical importance, little is known about their manufacture, as they have not been the subject of the same in-depth scientific studies as other cultural objects. In particular, the pigments used in their production remain largely unknown, as printers jealously guarded their know-how to prevent counterfeiting. We present here the results of an analysis of the pigments used in the printing of Swiss blue stamps produced between 1850 and 1908. They were studied non-invasively using a combination of Fourier transform infrared (FTIR) and Raman spectroscopy, which are particularly suitable in identifying natural pigments and synthetic dyes, notably in stamps [2-4].

Fig. 1: The first two federal stamps issues of Switzerland: Rayons I. The visible difference in colour is due to a change in printing process.

To date, only a small proportion of worldwide stamp production has been examined, and this is the first detailed study of Swiss stamps. It will not only benefit Swiss philately, but also provide information about the availability and cost of pigments, as well as the wider economic and cultural contexts that led to these choices. It will also aid in the detection of forgeries and the identification of counterfeits. The results obtained are put into perspective with those obtained on European stamps, enriching our knowledge of European stamp production in the 19th century and of the world economy at that time.

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Potential Response of Membrane-based Biosensor with Magnetic Charge Accumulation

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Biosensors can be read out by various methods ranging from optical to electrochemical principles. A major drawback from most of these techniques is that the sample needs to be altered to introduce a label, which make the bioassay lengthy and complicated. An obvious solution would be a direct electrochemical biosensor like such as the heparin sensor, which relies on a suitable membrane containing with tridodecylmethylammonium chloride as ion-exchanger and a low plasticizer content. [1] It is known that quaternary ammonium ions bind tightly to heparin, but other analytes of interest need a selective recognition element, which for larger biomolecules are often antibodies, aptamers and peptides. They exhibit a high selectivity and are immobilized on electrode surfaces to produce a signal, for example a current or a measurable potential change. [2-4] More recently, Lv et al. described a magneto-controlled potentiometric sensor based on selective peptide linked to a magnetic bead (MBs). [4] When the target is not bound, the peptide has large net positive charge which, when attracted to an ion exchanger containing membrane by the magnetic field, will induce a larger potential change compared to when the target is captured since its net charge is smaller. A magnetic field is used to concentrate the MBs on the membrane. The potential difference between the bound and unbound MBs-peptide is used as signal. However, this promising approach for potentiometric biosensor lacks a theorical understanding and characterization of the origin of underlying potential change. Indeed, Fu. et al. demonstrated that the membrane-based polyion sensor potential response is the consequence of a quasi-steady-state change that fades over time. [1] In the case of a magnetically driven charge accumulation no quasi-steady-state change should be present, except at the very beginning.

In this work we investigate the effect of magnetic charge accumulation of protamine modified MBs (0.74 µm) with a PVC based membrane surface on the potential change amplitude and over time. The plasticizer (dioctylsebacate) and ion-exchanger (potassium tetrakis(4-chlorophenyl)borate) concentrations are varied to study the influence of the hardness and resistance of the membrane on the potential. With the help of confocal microscopy, the penetration distance is characterized as a function of the membrane composition and is related to the potential change over time. Reversibility of the signal is tested by extracting the MBs with an opposite magnetic field.

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Submersible Probe for *In Situ* Ultrasensitive and Traceable pH Measurements

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Up to one-third of the anthropogenic atmospheric carbon dioxide diffuses into the oceans, altering the chemical equilibria in seawater [1]. This process is often referred to as ocean acidification (-0.002 pH y^{-1}) and is more pronounced in estuarine regions due to high organic matter concentration [1]. As pH controls many biogeochemical processes in aquatic environments, its monitoring is of great interest for a better comprehension of environmental systems [1]. Typically, pH is measured routinely with glass electrodes (Figure 1A). Their phase-boundary potential, measured at zero current against a reference electrode, relates to the sample pH following the Nernst equation. This intrinsic property results in a limited sensitivity that is insufficient for precise environmental pH monitoring.

Our group previously reported on an increased sensitivity for glass electrodes using an alternative readout called constant potential coulometry (Figure 1B) [2]. For this protocol, an electronic capacitor and a high impedance input voltage follower are implemented in the experimental setup and the cell potential is kept constant during the measurements. Thus, any potential change at the glass electrode induces an opposite one on the capacitor. The latter gives rise to a transient current from which the charge is obtained. This leads to an increased sensitivity compared to the classical readout. This setup was successfully applied with benchtop instruments to narrow pH ranges comparable to environmental samples with a precision of up to 64 µpH.

This work presents our efforts to implement this coulometric readout principle into a submersible probe for *in situ* measurements in aquatic systems. The electrodes are embedded in a flow system while also implementing electrochemical symmetry for better long-term accuracy (Figure 1C). The traceability chain is established for both freshwater and seawater.

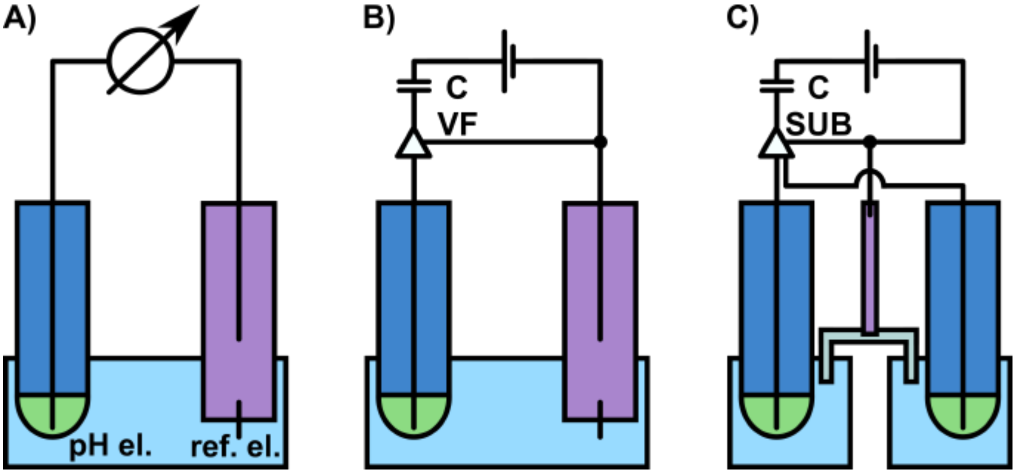

Figure1. A) Zero current potentiometry B) Coulometric readout with capacitor (C) and voltage follower (VF). C) Symmetrical coulometry with subtractor.

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Using Dynamic Electrochemistry to Trigger Optical Probes for Chemical Imaging

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Currently, there are few techniques for visualising ionic species in solution with spatial resolution while simultaneously providing information on their activity. These methods often require specialised equipment, are limited to a narrow range of analytes or suffer from low acquisition speeds. Such limitations make the study of dynamic systems particularly challenging. In this work, we introduce a new imaging platform that combines an optical reporter with a redox probe, allowing for the acquisition of spatially resolved chemical data of ionic species within seconds. The system is based on a molecule recently highlighted by our group for its remarkable redox properties. It is a lipophilic derivative of TEMPO, a stable aminoxyl radical that can be reversibly oxidised to its oxoammonium cation form.[1] Previous studies have reported that the radical form of TEMPO quenches the fluorescence of the rhodamine fluorophore.[2] By incorporating these two components into a thin ion-selective membrane (ISM) on the surface of an electrode, the oxidation of TEMPO mediates ion transfer between the membrane and the aqueous solution, maintaining electroneutrality in the organic phase. Simultaneously, it modulates the fluorescence signal of rhodamine, as its cationic form does not have the same quenching effect. This mechanism is schematically illustrated in Figure 1a. The application of a linear sweep potential results in the ion transfer wave that is directly coupled to the fluorescence intensity change with time, as shown in Figure 1b. Since the ion transfer potential depends on the ion activity in solution, the electrochemical conversion at different potentials triggers corresponding changes in the optical signal, which allows the visualisation of different ion activities on the same ISM.

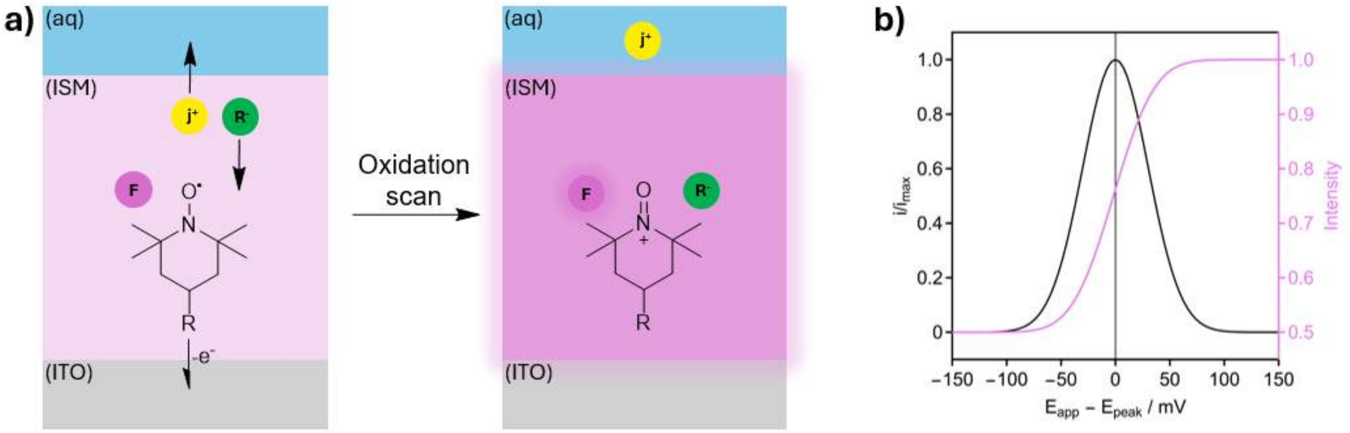

Figure 1. a) Schematic representation of the ion transfer mechanism between the membrane (ISM) deposited on the electrode surface (ITO) and the aqueous phase (aq) related to a fluorescence intensity change of the fluorophore (F). R^- represents a cation exchanger and j^+ a generic cation, **b)** Overlay of a simulated ion transfer wave (black curve) and a simulated fluorescence intensity change (magenta curve) as functions of the applied potential.

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Direct concentration (not activity) sensing of divalent cations

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Calcium metabolism is complex, and establishing its status by measuring Ca^{2+} levels in plasma, serum or urine can allow the diagnosis of bone disorders, parathyroid disease or chronic renal disease.

In clinical settings, potentiometric measurements are powerful diagnostic tools owing to the rapidness, reliability and operational simplicity of the technique. Potentiometry, in its simplest form, requires a two-electrode setup: A reference electrode provides a reference potential, which should be stable and independent of the sample composition, and is measured against an indicator electrode whose potential can be correlated to the *activity* of the analyte of interest. The activity depends on its concentration as well as on the ionic strength of the matrix, which itself is dictated by the different ionic species present and their respective concentrations.

Unfortunately, medical practitioners are trained to establish diagnostics based on ion concentrations, not activities. Depending on the required accuracy, it can be assumed that the ionic strength of a given matrix is constant, and therefore that the measured activities can be corrected in the same way for all sample into concentrations. But in some cases, the inter-individual variability in background electrolytes is not negligible, and removing the contribution of the ionic strength to the potentiometric measurements is of great interest. This is made possible by using a reference electrode whose potential is dictated by an ion of the same electronic nature as the ion of interest (measured by the indicator electrode). Bakker *et al.* already demonstrated the reliability of the principle for the direct concentration sensing of monovalent ions, such as nitrate using a silver / silver iodide reference electrode[1] and potassium using a tetrabutylammonium-based reference electrode[2].

This work investigates the synthesis and use of bis-quaternary ammonium salts as reference material for the direct concentration sensing of divalent cations such as calcium or magnesium.

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Covalent Attachment of Polyvinyl Chloride to a Clickable Self-assembled Monolayer on Gold Electrode for Selective Ion Sensing

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Solid-contact ion-selective electrodes (SC-ISEs) have shown substantial potential in various applications, including environmental monitoring, bioanalytical measurements, and wearable sensors. Typically, ion-selective membranes (ISMs) are applied to the electrode surface via drop casting of a cocktail containing sensing components such as ion exchangers, ionophores, and polymer substrates. Such SC-ISEs have demonstrated excellent ion response sensitivity, selectivity, and stability.[1] The thickness of such ISMs is generally on the tens of micrometer scale, resulting in relatively long preparation and conditioning time. Some studies have reduced the membrane thickness to tens or hundreds of nanometers using spin-coating, enabling quick ion sensing through either potentiometry or ion transfer voltammetry at the cost of limited lifetime and robustness.[2]

Self-assembled monolayers (SAMs) are well-ordered molecular layers that form spontaneously on substrates such as gold.[3] Thiol-gold interactions are commonly employed for substrate surface modification due to their ease of preparation and high stability, facilitating broad applications in biosensing, catalysis, nanofabrication, and electronics. These attributes make SAMs a possible tool for molecularly thin ion-selective membrane preparation.[3]

In our study, we utilized the thiol-gold interaction between thiol groups in 4-pentyne-1-thiol and the Au electrode to form a clickable self-assembled monolayer. A molecularly thin PVC layer was then covalently attached through the alkyne-azide click reaction between PVC-N_3 and the alkyne groups from the SAM. Sensing components such as ionophores, ion exchangers and plasticizers were incorporated, and thickness characterizations and performance evaluations were conducted using EQCM, potentiometry and ion transfer voltammetry. This molecularly thin film demonstrated excellent ion response performance, with significantly reduced thickness, shortening the conditioning time dramatically. Furthermore, when combined with a transparent conductive substrate, the thin sensing membrane also shows promise for optical sensing applications.

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A multi-modal analytical protocol for the characterisation of paintings at SIK-ISEA

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Paintings are highly heterogenous objects that combine organic and inorganic materials, both original and later additions - all in continuous exchange with the environment they are exposed to. The experimental nature and virtuosity of artists, combined with material degradation and the formation of alteration products over time, lead to additional complexity for analysts. Thus, understanding chemical processes and untangling complex material mixtures in multi-layered painted artworks requires a flexible analytical protocol to gain information on the components, the painting technique, the alteration and degradation products etc., using a combination of imaging and spectroscopic techniques from the macro to the submicron-scale.

The well-established collaboration of the Swiss Institute for Art Research (SIK-ISEA) in Zürich with the art-technological laboratory of the Hochschule der Künste Bern (HKB) merges the connoisseurship of art historians, restoration-conservation professionals, and heritage scientists. This collaboration gives access to non-invasive analytical approaches such as XRF mapping on large areas (tens of cm), reflectance spectroscopy and imaging, FTIR microscopy (external reflection mode), X-ray imaging and high resolution photography at SIK-ISEA, with minimally-invasive high-resolution methods for untangling the object stratigraphy at the micron and submicron-scale with sequential light microscopy, FTIR-FPA imaging [1], SEM, Raman spectroscopy [2] and GC-MS at HKB. Additional factors to be considered prior to the analytical characterisation of a painting are its conditions, including the logistics for non-invasive analysis, handling and selection of suitable sampling locations. Object size, type of support and condition of the artwork play also a crucial role in the choice of the analytical protocol to be followed.

Examples presented here include early 20th century works by Augusto Giacometti [3] and 18th century Indian paintings on paper from the Rietberg Museum collection.

A multi-modal and adaptable approach combining scientific photography, elemental mapping and spectroscopic data from the macro to the submicron-scale has shown to be a very effective way for the comprehensive study of such complex art objects.

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Advanced Non-Destructive Element-Sensitive 3D Tomography Using MIXE

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Muon-Induced X-ray Emission (MIXE) [1-4] is a non-destructive analytical technique that leverages negative muons to probe elemental and isotopic compositions by detecting characteristic muonic X-rays emitted during atomic cascades and gamma rays from nuclear capture processes. By controlling the muon beam momentum, MIXE enables depth-resolved analysis, spanning microns to centimeters, making it ideal for studying compositional variations in fragile, valuable, or operando samples. Significant advancements in MIXE technology have been achieved at the Paul Scherrer Institute (PSI) [5-7], facilitated by the high-rate continuous muon beam.

To further advance the technique towards a universal tomographic method, additional tracking information from incoming muons was integrated. Specifically, a Twin GEM-TPC (Gas Electron Multiplier-based Time Projection Chamber) tracker, initially developed for heavy-ion tracking at FAIR [8], was employed to enable precise measurement of muon trajectories. This advanced configuration facilitates the correlation of muon stopping points with X-ray emissions, thereby providing 3D information of the target and leading to the technique known as MIXE-Tomography (MIXE-T). Feasibility tests conducted at PSI using multi-layer targets have demonstrated the effectiveness and viability of this approach. This advancement establishes a foundation for element-sensitive imaging, positioning MIXE-T as a unique tool for high-resolution, depth-specific elemental analysis across a broad range of scientific applications, including cultural heritage.

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Advantages and Limitations of Reference Electrodes based on Organic Electrolytes

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In the 21st century, tremendous effort in academia and industry has been focused on the development and commercialization of sensing platforms and analytical devices for non-invasive detection and monitoring of disease biomarkers [1]. This ambitious pursuit brought forth advancements in electrochemical recognition mechanisms while simultaneously highlighting the need for innovative solutions in reference element design. Double-junction reference electrodes (REs), though tried and tested, are cumbersome to miniaturize owing to their inner compartments with the reference solution and the bridge electrolyte, whereas frequently used Ag/AgCl-based quasi-reference elements rely heavily on the constant Cl^- concentration in the sample. Liquid junction-free REs provide a promising alternative by using "water-immiscible salt bridges" such as free-flowing ionic liquids (ILs) or membranes doped with organic electrolytes. Upon contact with a sample, these electrolytes partition into the aqueous phase (Fig. 1a), forming an equilibrium distribution and a phase boundary potential largely unaffected by sample composition (Fig. 1b, red circles). Despite their simplicity and miniaturization potential, however, the lack of understanding of their limitations has hindered widespread adoption [2].

This study explores polymeric membrane REs based on organic electrolytes. Through theory and experiments, we reveal key limitations linked to electrolyte lipophilicity. Low-lipophilicity electrolytes are prone to ion-exchange interference (Fig. 1b, green circles) and suffer from salt leaching, shortening membrane lifetimes [3]. In turn, highly lipophilic electrolytes require precise cation-anion matching control, as even minor impurities lead to potential deviations. To overcome these issues, we propose a novel principle combining a highly lipophilic electrolyte and an ionophore, achieving stable electrode potentials (Fig. 1c) with minimal leaching.

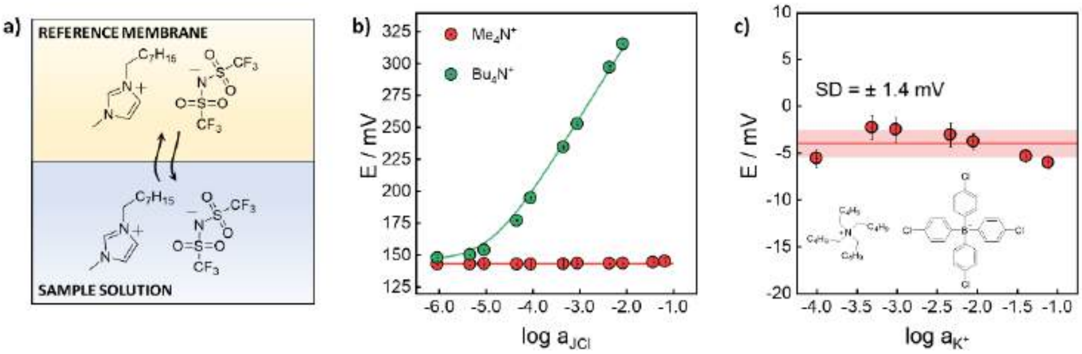

Figure 1. a) Partitioning of the IL $[C_8mim^+][C_1C_1N^-]$ between the membrane and the sample; b) response of the corresponding REs to tetraalkylammonium chlorides of varied lipophilicity; c) K^+-response of REs based on the lipophilic salt $TPA^+TpClPB^-$ and valinomycin.

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