

A DOUBLE CHEMFET FLOW CELL SYSTEM FOR DETECTION OF HEAVY METAL IONS AND INTEGRATION IN μ TAS

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0. Abstract

A new type of flow cell has been developed for detection of heavy metal ions in aqueous solutions, based on the flow injection method. The cell contains two chemically modified field effect transistors (CHEMFETs) of which one is selective for the supporting electrolyte ion (in this case a 0.1 M potassium ion solution) and the other is selective for the heavy metal ion to be detected (Cd^{2+} , Pb^{2+}). The differential signal of the reference electrode CHEMFET and the heavy metal ion CHEMFET in the flow cell system which has been presently developed will be evaluated for miniaturization and further integration in a micro total analysis system.

1. Introduction

A chemical sensor connects the chemical domain and the physical domain. Our work is aimed at the design and synthesis of molecular receptors that can selectively recognize a guest species, and the development of sensor systems that incorporate these receptors. When the guest species complexed by the receptor are charged, like cations, the chemical recognition process converts a neutral receptor into a charged species. This allows the potentiometric detection by use of chemically modified field effect transistors for the transduction of the (chemical) complexation reaction into an electronic signal. These sensors can provide direct information for localisation of environmental pollution and can be applied in water quality monitoring, biomedical analysis and biomonitoring. The innovative technology from the semiconductor materials, micro-engineering, sensor and molecular engineering world shows great promise for the development of microsensors for the fabrication of multi-ion sensors by IC technology. Miniature CHEMFETs compatible with IC techniques have been developed in our group recently and applied in a flow cell [1].

2. CHEMFETs for the detection of ion activities

The CHEMFET is a special modification of the ion sensitive field effect transistor (ISFET) in which the gate oxide is covered with an ion selective membrane [2]. The ion selectivity is introduced by incorporation of ion-selective receptor molecules in a hydrophobic polymer membrane. Between the sensing membrane and the gate oxide of the ISFET a buffered hydrogel is introduced which serves as inner electrolyte solution and eliminates pH sensitivity and CO₂ interference (Figure 1) [3].

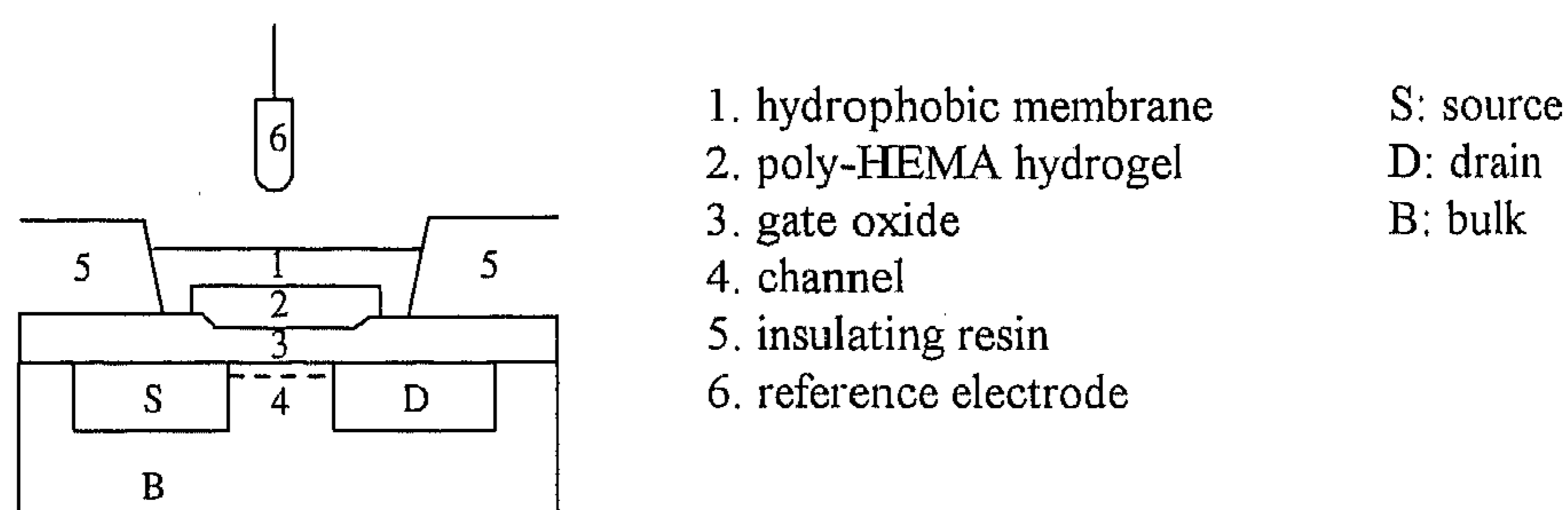


Figure 1. Schematic representation of a CHEMFET.

The selectivity of the CHEMFET is determined by the selectivity of the ion receptor in the sensing membrane, the partition coefficients of the different ions over the membrane and aqueous phase, and the relative concentrations of the ions in the sample solution. An important part of our sensor research is directed to the design and synthesis of ion receptor molecules which have a high selectivity towards common interfering ions. The use of calix[4]arenes as molecular building blocks has proven to be particularly versatile in this respect, because functionalization of the phenolic oxygens in the cone conformation offers the unique possibility to orient four ligand chains at the same side of the molecule. Moreover, these molecules have a high lipophilicity when gives them a high affinity for the membrane phase. Using calix[4]arene as building blocks, highly selective receptors have been developed for potassium, silver, lead, cadmium and a number of other cations[4-6]. For testing their performance in CHEMFETs, these receptor molecules were incorporated in plasticized PVC membranes. An illustration of the excellent response of CHEMFETs containing a calix[4]arene-based silver and lead receptor, is given in Figure 2.

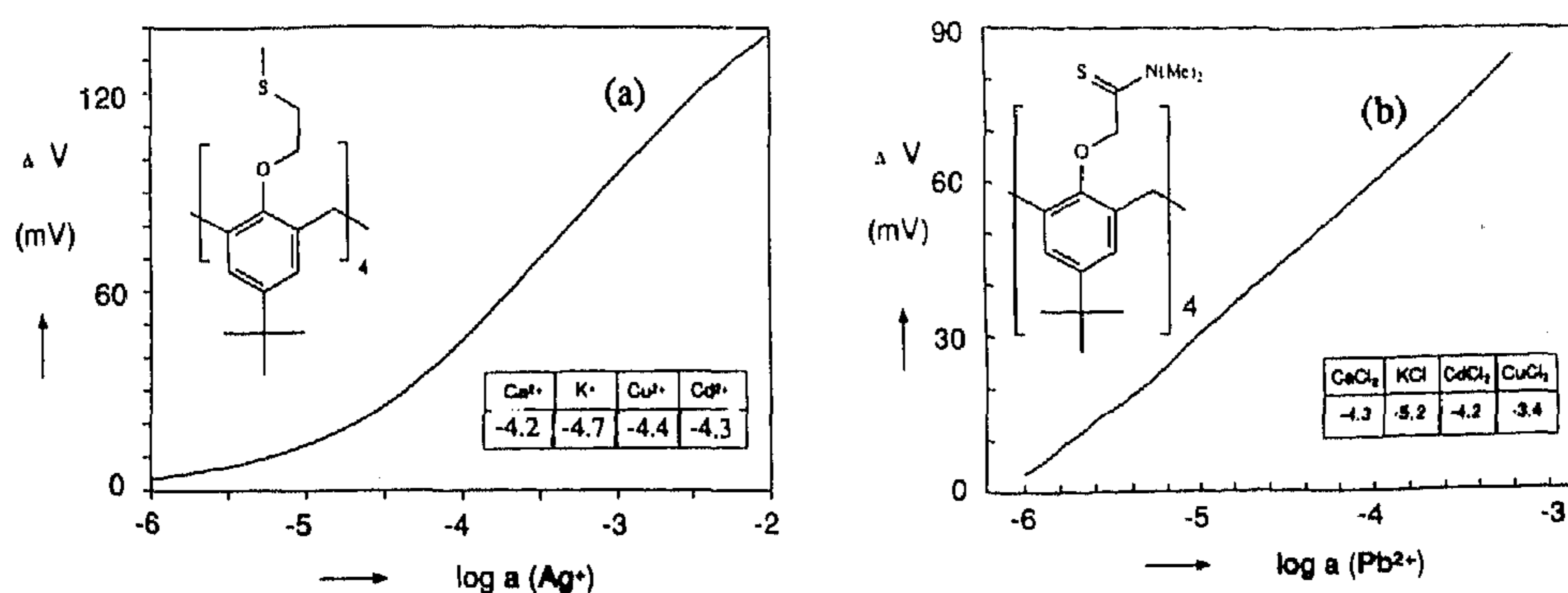


Figure 2. Response of Ag^+ -selective CHEMFET (a) and Pb^{2+} -selective CHEMFET (b) in the presence of 0.1 M $\text{Ca}(\text{NO}_3)_2$ and 1 M KCl , respectively. Inset: Selectivity coefficients in the presence of 0.1 M interfering ion.

3. Development of a double CHEMFET flow cell system

Due to their small dimensions, chemically modified field effect transistors are particularly useful for application in flow sensor systems. A double sensor flow-through cell has been developed for detection of heavy metal ions in aqueous solutions (Figure 3). The cell contains two CHEMFETs of which one is selective for the supporting electrolyte ion (in this case a 0.1 M potassium ion solution) and the other is selective for the heavy metal ion to be detected (Cd^{2+} , Pb^{2+}).

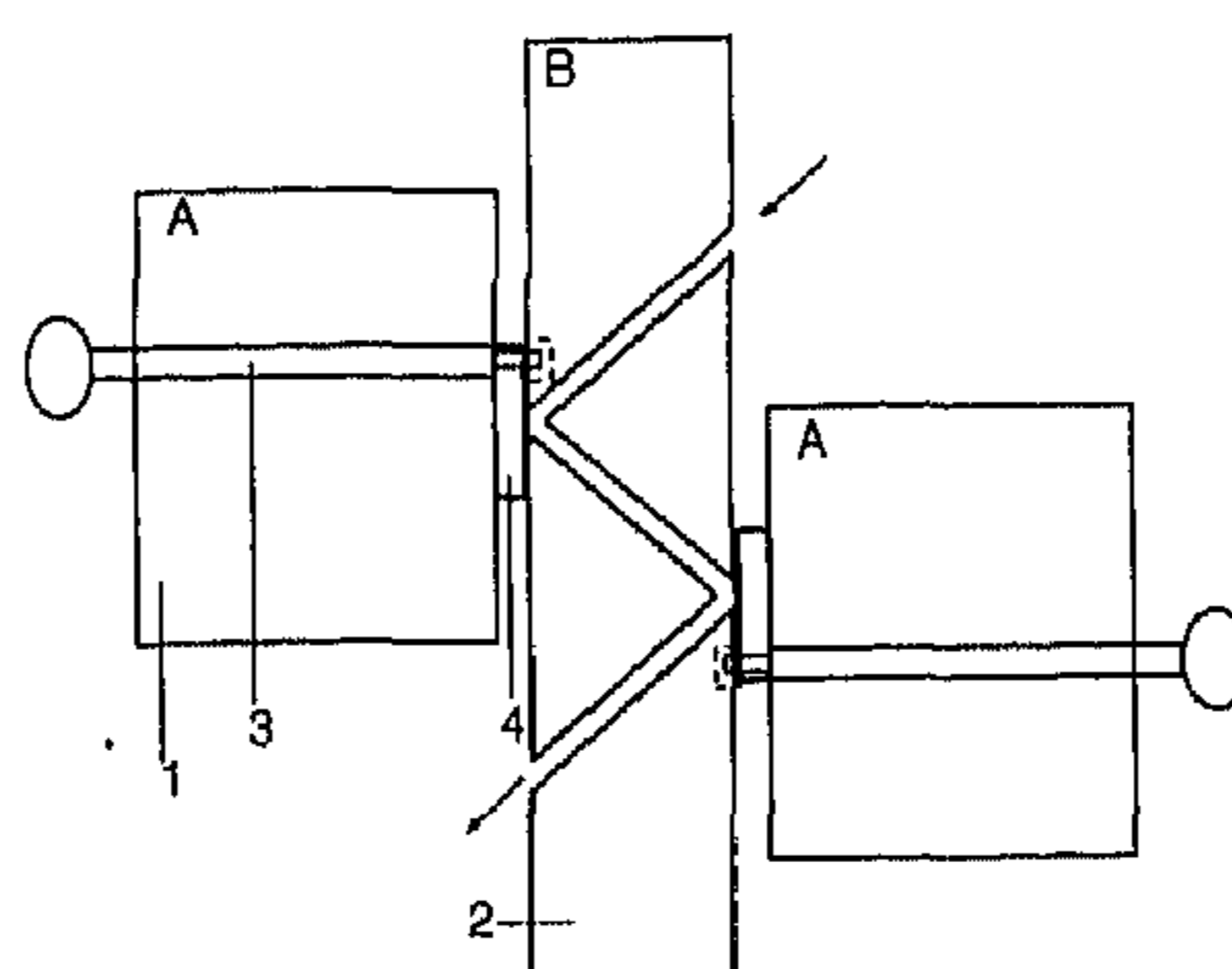


Figure 3. Side view of the detailed structure of the double sensor flow-through cell: perspex (1,2), contact wire (hook) (3), CHEMFET (4).

The differential signal of the reference CHEMFET and the heavy metal ion CHEMFET in the flow cell yields a stable signal, free of drift and noise effects (Figure 4).

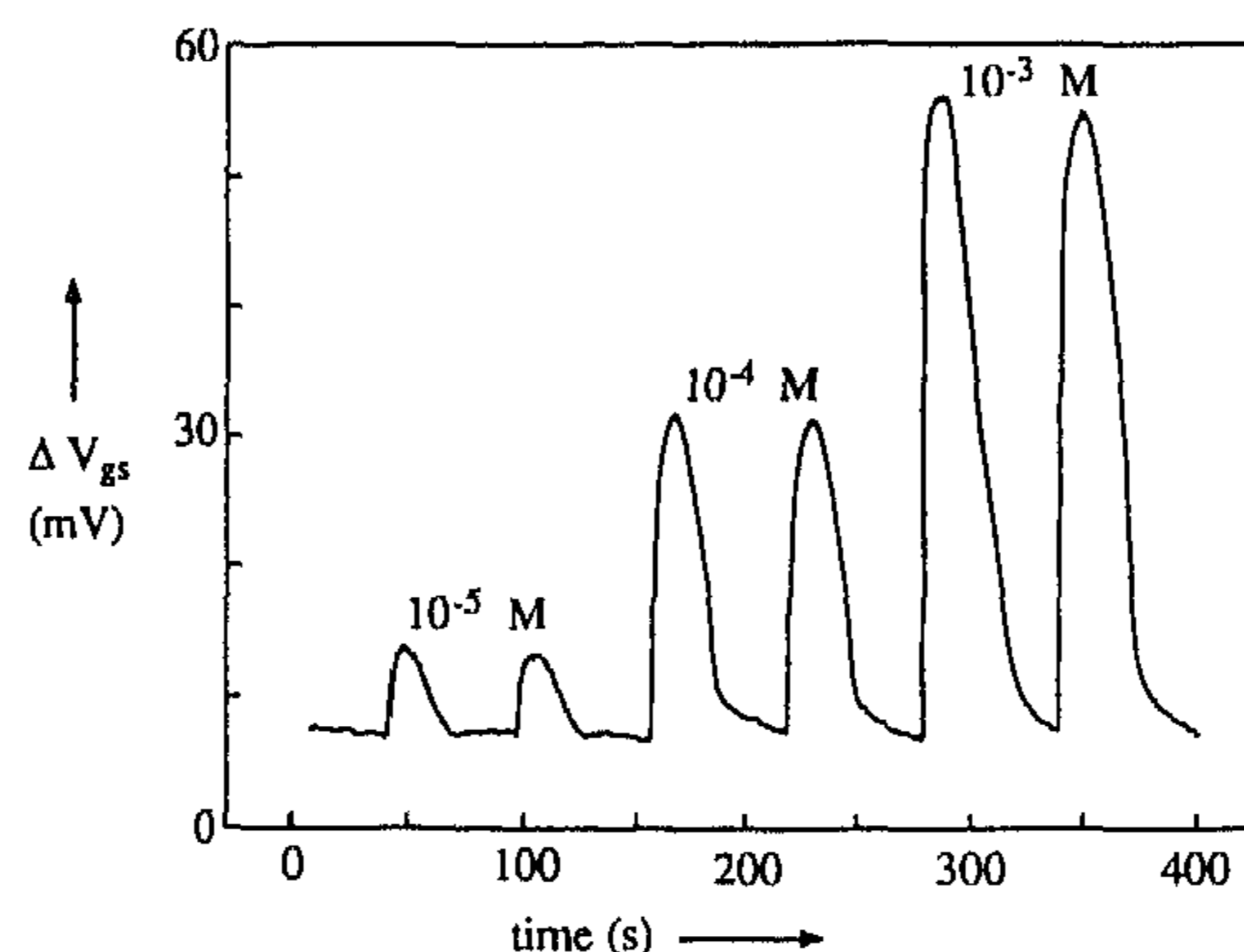


Figure 4. Response of Pb^{2+} CHEMFET measured differentially with respect to K^+ CHEMFET in the double sensor flow-through cell. ($Q = 1.1 \text{ mL}\cdot\text{min}^{-1}$; carrier: $10^{-6} \text{ M PbCl}_2 + 100 \text{ mM KCl}$; injection: $PbCl_2 + 100 \text{ mM KCl}$; $V_i = 220 \mu\text{L}$).

4. Implementation of durable sensors in total analysis systems

A further step in miniaturization results in a micro total analysis system [7]. When incorporated in such a system, the requirements for the properties of the CHEMFETs change. First of all, the design of the CHEMFET must be in accordance with the micro fluid system as presented in [8]. Furthermore, drift is less critical, because automatic calibration can easily be incorporated in the micro system. On the contrary, the durability becomes more important if a continuous stand-alone operation of the μTAS is required.

Although plasticized PVC membranes with ionophores as sensing membranes give already quite satisfactory results for a limited period of time, the adhesion of the membrane is not stable and plasticizer and ionophore leach out from the membrane upon prolonged contact of the sensor with the aqueous solution. A sensor of practical use in a total analysis system must have a long lifetime, which requires the covalent attachment of the sensing membrane to the semiconductor surface. Also electroactive components in the sensing membrane must be prevented from leaching out, which can only be achieved by covalent attachment. Therefore a new membrane material has been developed to which the electroactive components, *viz.* the selective receptor and the anionic site, can be covalently bound. An example of such a modified CHEMFET architecture for detection of K^+ is depicted in Figure 5. Due to the covalent linkage of the ionophore via the methacrylate group leaching out from the membrane matrix is prevented and a stability of several months for the sensor in flow cell is obtained. In contrast, membranes with the same ionophore but without covalent attachment lose their activity quickly (Figure 6). In principle the above described architecture is generally applicable for the detection of charged species which can build up a membrane potential.

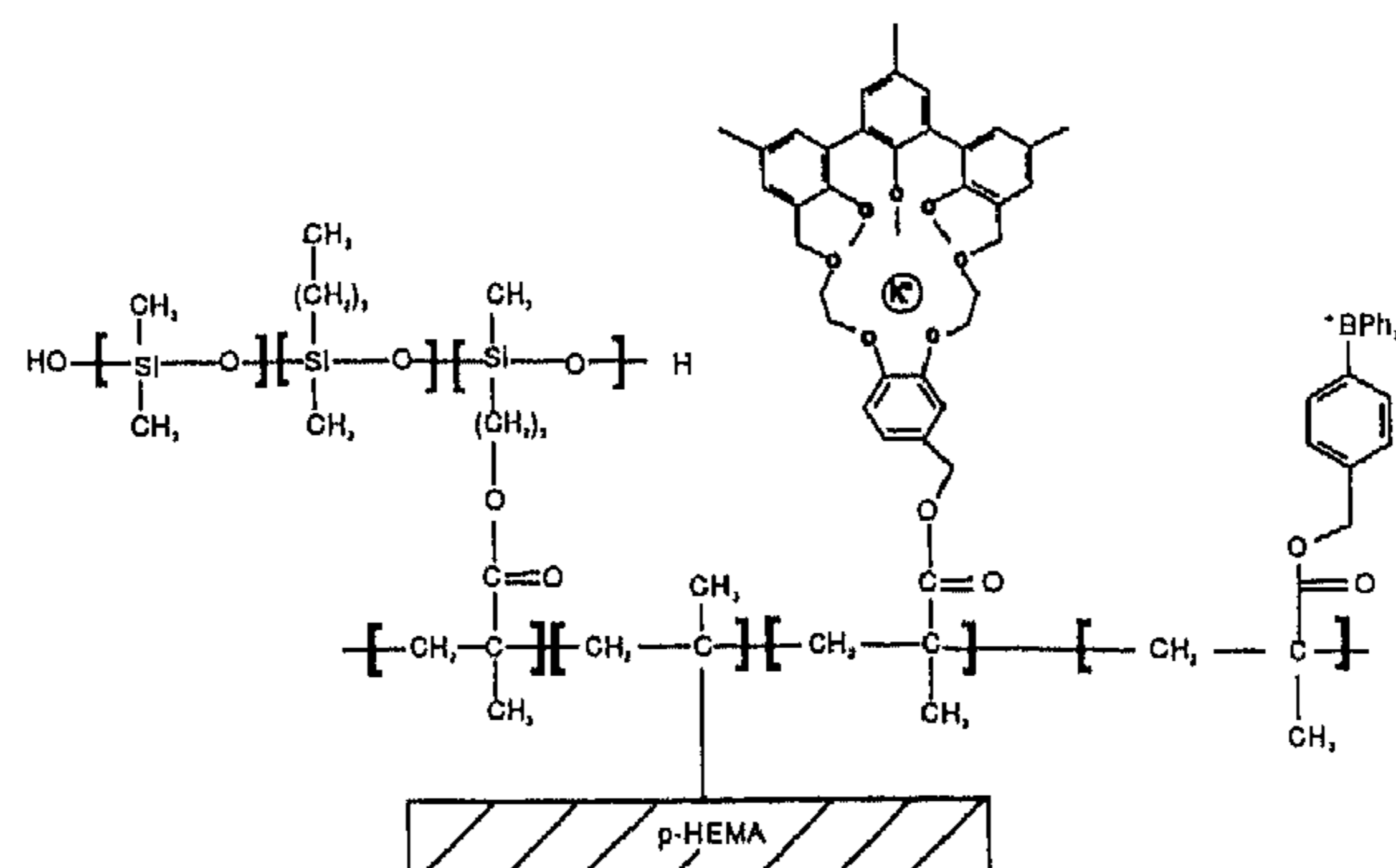


Figure 5. Schematic representation of the sensing membrane after photocrosslinking.

Currently we are also investigating the effect of covalent immobilisation of different ion receptors for heavy metal ions, which can be used in a micro flow system and can be implemented in a total analysis system circuit.

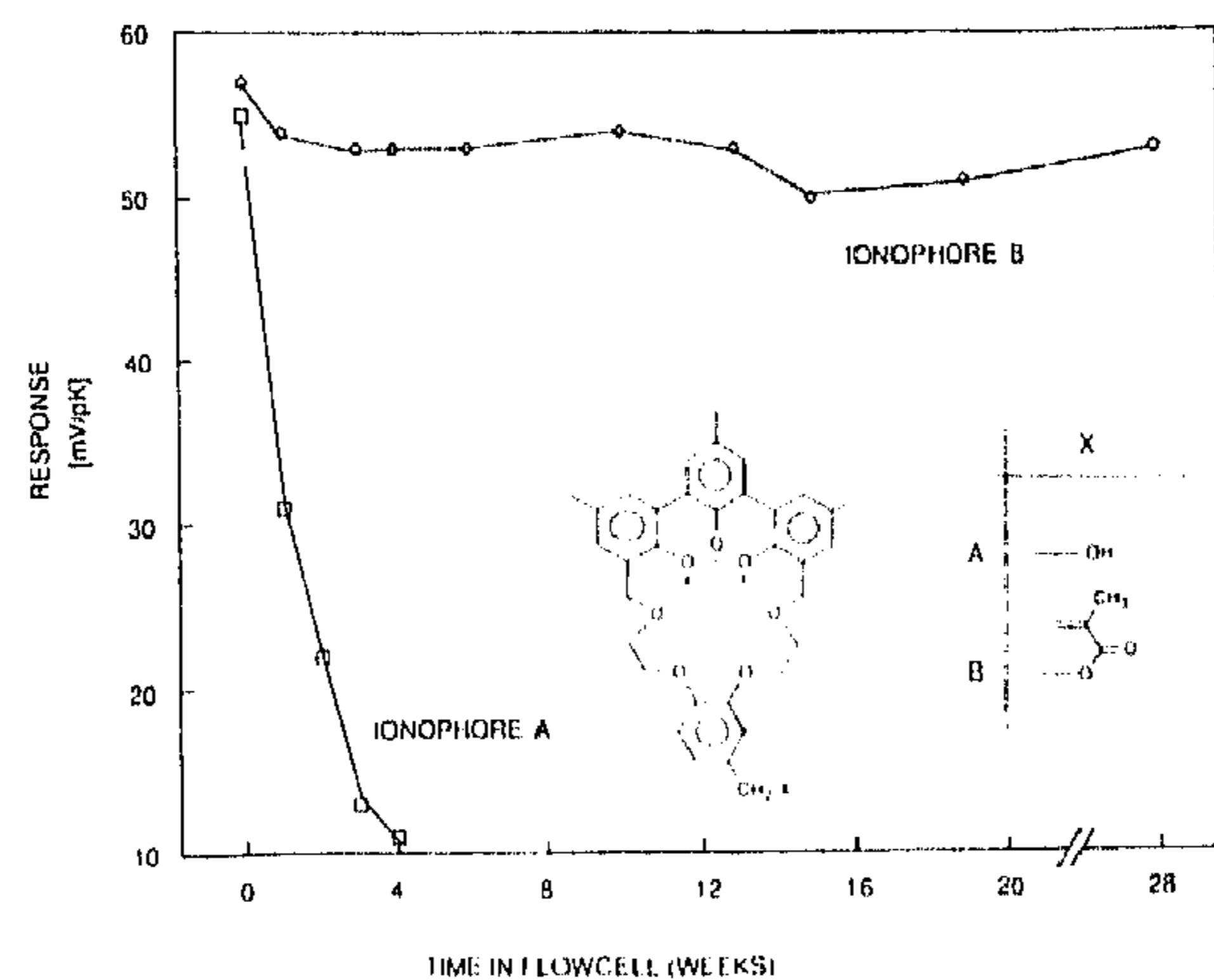


Figure 6. Sensor response characteristic in time. A: ionophore without covalent attachment. B: ionophore with covalent attachment.

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