

## COMPARING DIFFERENT APPROACHES FOR ASSEMBLING SELECTIVE ELECTRODES FOR HEAVY METALS

Iva Turyan, Meirav Atiya, Galit Shustak and Daniel Mandler

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904

Different approaches for increasing the sensitivity and selectivity of voltammetric probes for heavy metals will be presented. These involve the application of adsorbed monolayers of host molecules, functionalized self-assembled monolayers, thin polymeric films and template-based sol-gel films. Two systems have been examined that focus on the selective analysis of Hg(II) and Fe(II). The electrode for Hg(II) is based on a macrocyclic ligand, i.e., Kryptofix-222, while that for Fe(II) relies on the selective complexation by ferriox ligands, such as 1,10-phenanthroline. The monolayer and polymeric approaches have been tested and compared for both systems. We found that basically, an interface comprising a monolayer, which is capable of forming a strong and selective complex with the analyte, is likely to exhibit sensitivity that is at least as good as a polymeric film. On the other hand, the stability and durability of the latter usually makes it a superior interface for repetitive analysis and will therefore be the preferred choice for flow analysis systems.

In addition, a template-based approach for introducing sensitivity and selectivity in electrochemical probes has been examined. The method is based on the formation of a sol-gel matrix in which the analyte, i.e., the template, is entrapped, followed by its removal. Specifically, a glassy carbon electrode spin-coated with silica sol has been used for the analysis of iron(II) ions. The silica sol was prepared from a hybrid mixture of phenyltrimethoxysilane and tetraethoxysilane, long alkyl chain alkylsulfonate, i.e., dodecanesulfonate, and the template molecule, i.e., trisphenanthrolineiron(II),  $\text{Fe}(\text{phen})_3^{2+}$ , complex.  $\text{Fe}(\text{phen})_3^{2+}$  was extracted from the dried film by electrocycling the modified electrode in an iron-free solution. After removal of the complex, complementary binding sites for the template remained. The molecular recognition properties of these synthetically designed binding sites toward

$\text{Fe}(\text{phen})_3^{2+}$  complex were elucidated further using cyclic voltammetry (CV).

It is evident that film porosity as well as hydrophobic/hydrophilic and electrostatic interactions play an important role in controlling molecular permeation through these materials. The advantages of sol-gel technology, such as mild polymerization, allow specific analytes to be readily introduced with the highly cross-linked, porous host structure.