Application of Adsorptive Stripping Voltammetry for Indirect Measurement of Nonelectroactive Ions Using Competitive Complex Formation Reactions

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Abstract. It is shown that adsorptive stripping voltammetry can be used for indirect determinations of non-electroactive species. Determination of fluoride was selected to demonstrate this concept which can be used in environmental, clinical and other applications.

The fluoride determination is based on competitive complex formation reactions between zirconium and organic ligands, viz. Alizarin Red S (ARS) and Acid Alizarin Violet N (AAVN) and fluoride ions in acidic media (0.1M HNO₃ or HClO₄). Free ARS ligand is adsorbable on mercury electrode and its voltammetric peak increases with fluoride concentration due to ARS displacement from the Zr-ARS complexes with fluoride forming more stable Zr-fluoride complexes. Using AAVN as a ligand Zr-AAVN complexes are adsorbable on a mercury electrode and the voltammetric peak decreases with increasing fluoride concentration due to formation of more stable Zr-fluoride complexes.

The sensitivity of the method is down to 0.1 μM of fluoride. Overall fluoride recovery from synthetic water samples at micromolar concentration level was within 1% of the concentration added, with overall reproducibility of 5 independent measurements of ± 2.5% and ± 1.8% with ARS and AAVN ligand, respectively. Some interferences possibly present in water have been investigated.

Key words: adsorptive stripping voltammetry, fluoride determination, zirconium determination, zirconium complexes, Alizarin Red S, Acid Alizarin Violet N.

Stripping voltammetry (SV) offers many advantages being one of the most sensitive electroanalytical techniques [1–3]. This technique requires relatively simple and inexpensive instrumentation which can be used even in environmental field appli-
cations, in most cases it is very selective and its detection limit is at about $10^{-12}$ M. The inherent sensitivity of SV is attributed to the coupling of an effective pre-concentration step and advanced voltammetric waveforms imposed to the working electrode of electrochemical cell [4].

Electrolysis and interfacial accumulation are the most important processes used in electrolytic and adsorptive SV, respectively. The main advantage of the latter compared to the former technique is that the application of adsorptive SV can be extended to the determination of non-amalgam forming species. Many adsorbable electroactive organic and biochemical compounds have been determined directly by this technique [5]. The technique has also been used for the determination of many metal ions using adsorption of metal ion complexes with organic ligands [5] which are well-known UV/VIS spectrophotometric reagents. [6]. Adsorptive SV has, however, some advantages compared to UV/VIS spectrophotometry: by working at much lower concentrations of ligand the problems associated with low solubility or absorptivity, often encountered in spectrophotometry, are avoided in adsorptive SV. At the same time adsorptive SV can be used to determine significantly lower concentrations of metal ion using the same ligand. The most important prerequisite for some organic ligand to be used in adsorptive SV is its (or its metal ion-complex) adsorbability at the electrode surface using selected experimental conditions.

In this paper the scope of adsorptive SV is extended to the indirect determination of trace levels of non-electroactive ions based on the judicious choice of competitive complex formation reactions. The determination of low levels of fluoride is used to illustrate this concept which can be applied to many other systems. Our model procedure is based on the displacement of zirconium from zirconium-Alizarin Red S and zirconium-Acid Alizarin Violet N complexes by fluoride ion forming in acidic medium more stable zirconium-fluoride complexes [7].

Fluoride is used as a model analyte because of its significant environmental and clinical impact [8, 9]. Fluoride is commonly measured by fluoride selective electrodes [10] or AA spectrometry [11, 12], but the inherent sensitivity of the adsorptive SV enables development of the procedure for convenient measurement of submicromolar fluoride concentrations.

**Experimental**

**Apparatus**

All measurements have been made at room temperature air conditioned to 21°C, using computerized BAS 100A electrochemical analyzer (Bioanalytical System, Inc., USA) coupled with a static mercury drop electrode (SMDE) model 303A, an electromagnetic stirrer model 305 (both EG & G Princeton Applied Research, USA) and HIPLOT plotter model DMP-40 (Houston Instrument, USA). Nitrogen purging, stirring and mercury drop dispense/dislodge have been controlled by the BAS 100A computer system.

Linear sweep SV on a large drop size on SMDE 303A with potential scan rate of 50 mV/s has been used throughout all experiments.

**Chemicals**

Stock solutions at 10 mM concentration level of p.a. grade zirconium nitrate and sodium fluoride were prepared and daily diluted to 0.1 mM for further dilution.