

FEATURES AND CONDITIONS FOR SUBTRACTIVE ASV USING SILVER AND GOLD ELECTRODES

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Underpotential deposition (UPD) plays a central role in the deposition and dissolution steps of anodic-stripping voltammetry (ASV) [1,2,5]. During the deposition step, the adatom coverage of trace elements is in the range of 0.01 - 1 % and no bulk deposition is invoked for metals that exhibit underpotential deposition (e.g. Pb and Cd on Ag; Hg, Cu and Pb on Au). In these cases, the UPD properties of the deposit are the main factor that determines the analytical characteristics of the method.

Several unusual features are related to the UPD phenomenon.

(i) It is substantially easier to determine mercury on gold in the nanomolar range (by ASV) than in the millimolar range with the use of steady state methods [5]. The reason for this is that no structural changes of gold take place during ASV (which is UPD controlled), while for steady-state methods, amalgamation of the gold, occurring at high concentrations, requires repolishing of the electrode prior to each run. In addition it is necessary to remove oxygen.

(ii) Manipulating the UPD properties may enable the determination of an analyte at trace concentration in the presence of a large excess of a more easily reducible metal ion [1,6]. For this purpose, the right substrate must be chosen at which the trace metal exhibits underpotential deposition, while the metal in excess does not. The metal in large excess forms a three-dimensional lattice, without occupying the entire electrode surface, and leaves enough space for the formation of a uniformly distributed sub-monolayer of the analyte. The efficiency of this approach was demonstrated with the determination of lead [1] and cadmium [6] in the presence of a 10000-fold excess of Cu^{2+} on a silver electrode. Were it not for the UPD, the deposits of Pb and Cd would be buried in the copper deposit and, as a consequence, would not be stripped quantitatively in the potential range that characterizes each element.

The silver electrode exhibits excellent characteristics for lead [2], high repeatability (better than 2% at 1 nM Pb^{2+}) and long-term stability without requiring any pretreatment (Fig 1a). The performance is less good for Cd^{2+} [6]. The conditions required are use of a non-isolated silver counter electrode and working in solutions from which oxygen has not been removed. A mechanism of continuous renewal of the silver electrode is proposed. Electrochemically pretreated gold electrodes exhibit excellent features for mercury [5] (Fig 1b).

In order to ensure a suitable environment for the determination of subnanomolar concentrations, the following is recommended: (i) Applying the SASV mode of ASV (Fig. 2) [2-6]. (ii) Not removing oxygen [1-6]. (iii) Working in a 2-electrode system when possible [1,3,6]. (iv) Adding the standard additions in rapid sequence [1-6].

μ Autolab GPES-software was found to be suitable for this purposes.

SASV is carried out by making background correction, which is subtracted, from the original ASV [3]. The pseudo background is obtained by recording an ASV with zero deposition time immediately after the original ASV. The pseudo background curve permits a more accurate representation of the state of the electrode than does a conventional background curve taken in the supporting electrolyte only. The reason for this is that the variations which can occur on the electrode during solution exchange are considerably larger than those occurring with the recording of the pseudo background without changing the solution. This compensates for continuous changes occurring in the background at high sensitivities. The improvement achieved by the SASV can be seen in Fig.2.

The method has been applied to the determination of Pb^{2+} [1,2,6] and Cd^{2+} [6] on silver with detection limits of 50 pM and 1 nM respectively at 90 s deposition time and for Hg^{2+} [4,5] and Cu^{2+} [2,5] on gold with detection limits of 50 and 100 pM respectively at 120 s deposition time. The matrices studied were drinking, river and sea water, heavily polluted water and urine.

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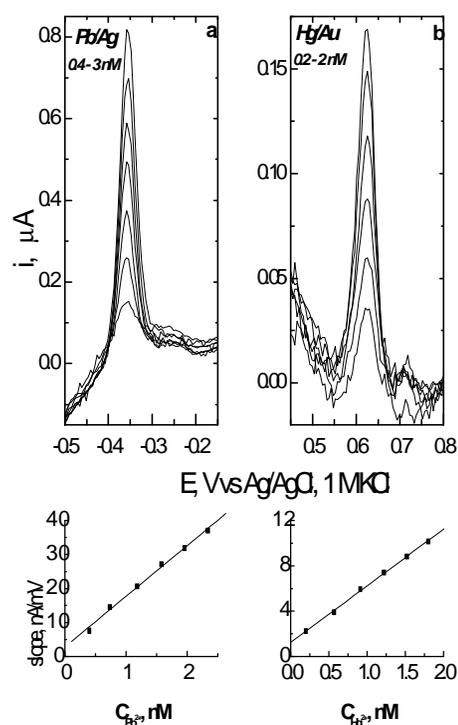


Fig 1(a) SASV of Pb^{2+} at Ag/RDE and (b) SASV of Hg^{2+} at Au/RDE
 $t_{\text{dep}} = 90$ s for Pb^{2+} and 180 s for Hg^{2+} .

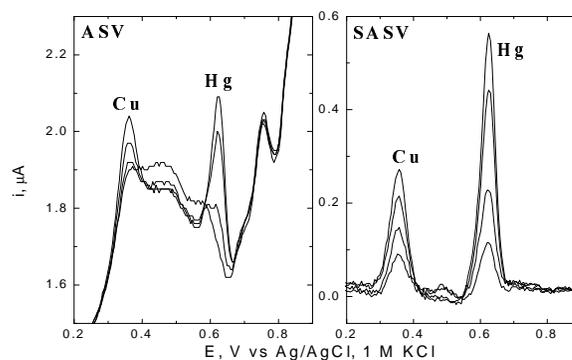


Fig. 2 ASV and subtractive ASV, at Au-RDE.
 4, 8, 12 and 20 nM Hg^{2+} and 5, 10, 15 and 20 nM Cu^{2+} .
 $t_{\text{dep}} = 30$ s; SW mode.