

# ELECTROCATALYSIS IN STRIPPING VOLTAMMETRY OF SULFUR COMPOUNDS

F. G. Bănică<sup>1</sup>, Ana Ion<sup>2</sup>, Nicolae Spătaru<sup>3</sup>, and Tanța Spătaru<sup>3</sup>

*1) Dept. of Chemistry, Norwegian Univ. of Science and Technology, Trondheim, Norway*

*2) Dept. of Analytical Chemistry, University Politehnica of Bucharest, Romania*

*3) Romanian Academy, Institute of Physical Chemistry, Bucharest, Romania*

## Abstract

This contribution reviews some applications of electrocatalysis in indirect stripping voltammetry of electrochemically inactive sulfur compounds that are not amenable to the detection by direct electron transfer reactions.

As a first example, ligand-catalyzed metal ion reduction on a mercury electrode will be dealt with<sup>1</sup>. Electrocatalysis of Ni(II) or Co(II) reduction by compounds like cysteine and its derivatives as well as other thiol derivatives (penicillamine, mercaptopurine derivatives) enables the sensitive detection of the ligand itself. The analyte can be accumulated either as an adsorbed nickel complex or as a sparingly soluble mercury salt, according to the accumulation potential and the stability of the nickel complex. The occurrence of two different accumulation mechanisms enables much flexibility when dealing with interferences.

Second, catalytic hydrogen evolution in the presence of Co(II) and sulfide ion will be approached, with a focus on the determination of sulfide ion at the trace level<sup>2a</sup>. The same electrode process can be employed for the determination of sulfur organic derivatives that generate sulfide ions by a chemical reaction during the pre-concentration step on a mercury electrode<sup>2b,c</sup>.

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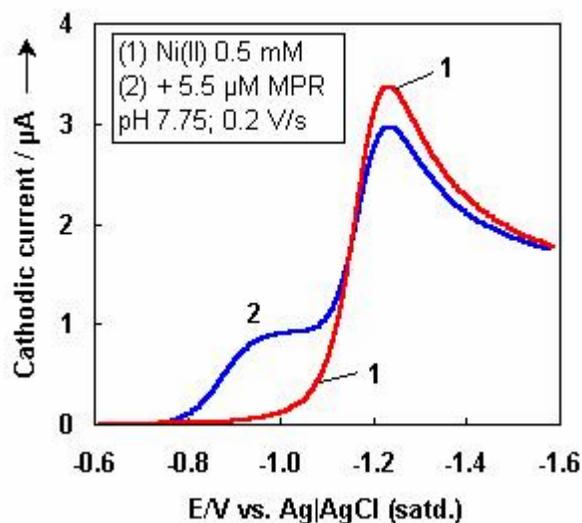
<sup>1</sup> a) F. G. Banica J. C. Moreira and A. G. Fogg, *Analyst*, **1994**, *119*, 309; b) F. G. Banica, A. G. Fogg, A. Ion and J. C. Moreira, *Analyt. Lett.*, **1996**, *29*, c)1415. A. Ion, F. G. Banica, A.G. Fogg and H. Kozłowski, *Electroanalysis*, , **1996**, *8*, 40; d) A. Ion, F. G. Banica, C. Luca, *Electroanalysis*, **1997**, *9*, 945

<sup>2</sup> a) F. G. Banica, N. Spataru and T. Spataru., *Electroanalysis*, **1997**, *9*, 1341; b) F. G. Banica and N. Spataru, *Talanta*, **1999**, *48*, 491; c)N. Spataru and F. G. Banica; *Analyst*, **2001**, *126*, 1907.

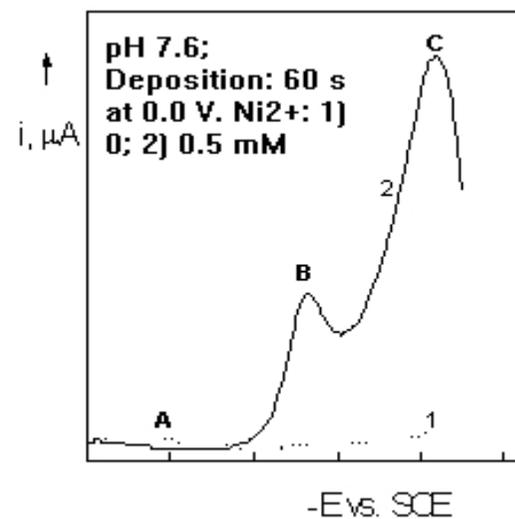
# 1. Metal-ion catalytic prewave at the HMDE: an example

Metal ion:  $\text{Ni}^{2+}$ ; Ligand-catalyst: mercaptopurine-riboside (MPR)

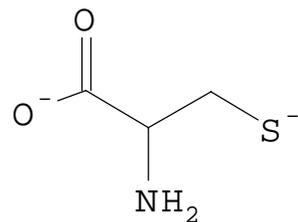
Linear scan voltammetry



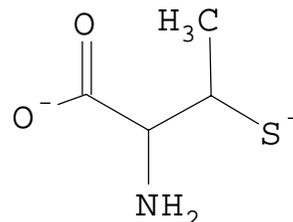
Cathodic stripping voltammetry  
(20 nM MPR)



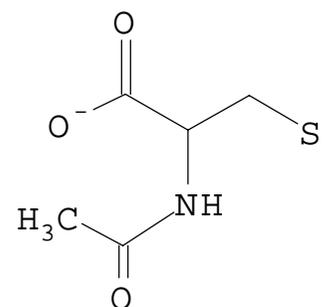
## 2. Metal-ion catalytic prewave: typical ligands



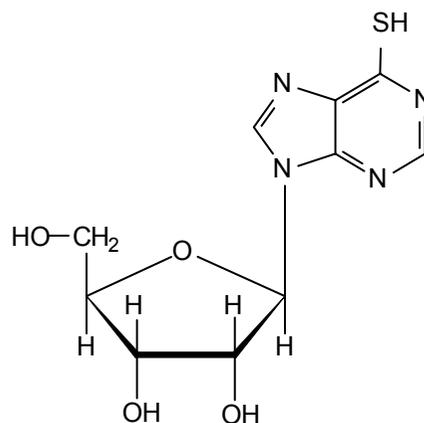
Cysteine



Penicillamine

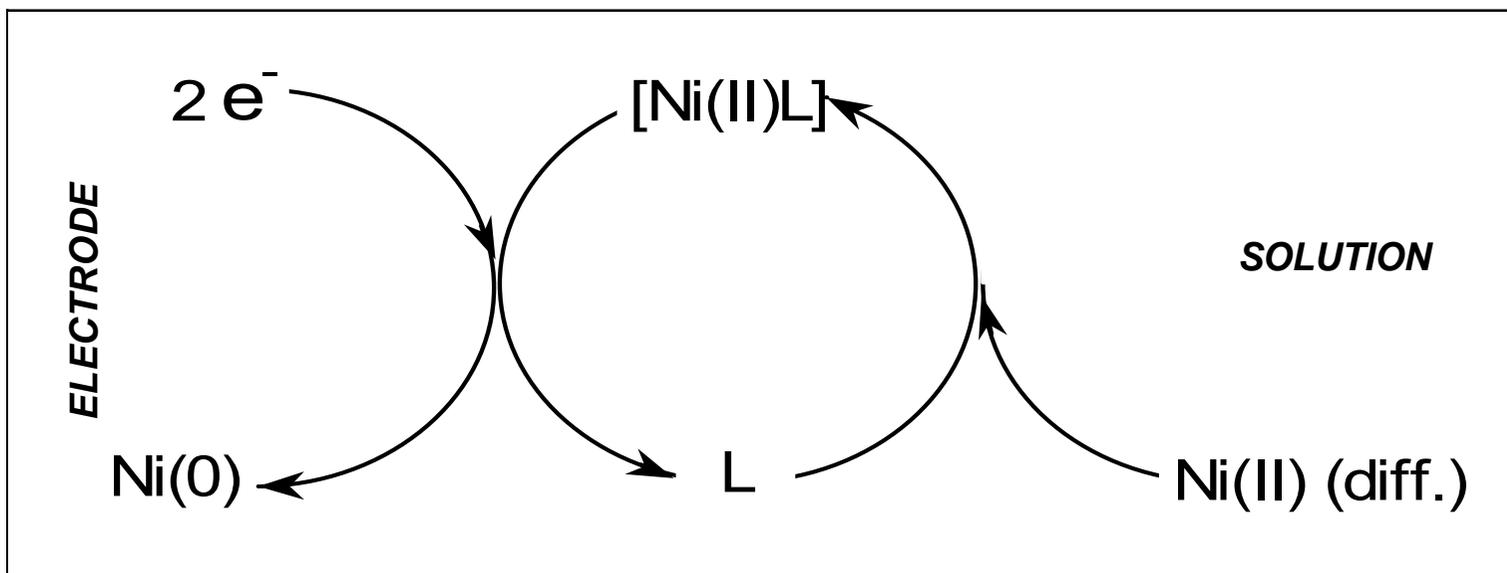


N-acetyl-cysteine



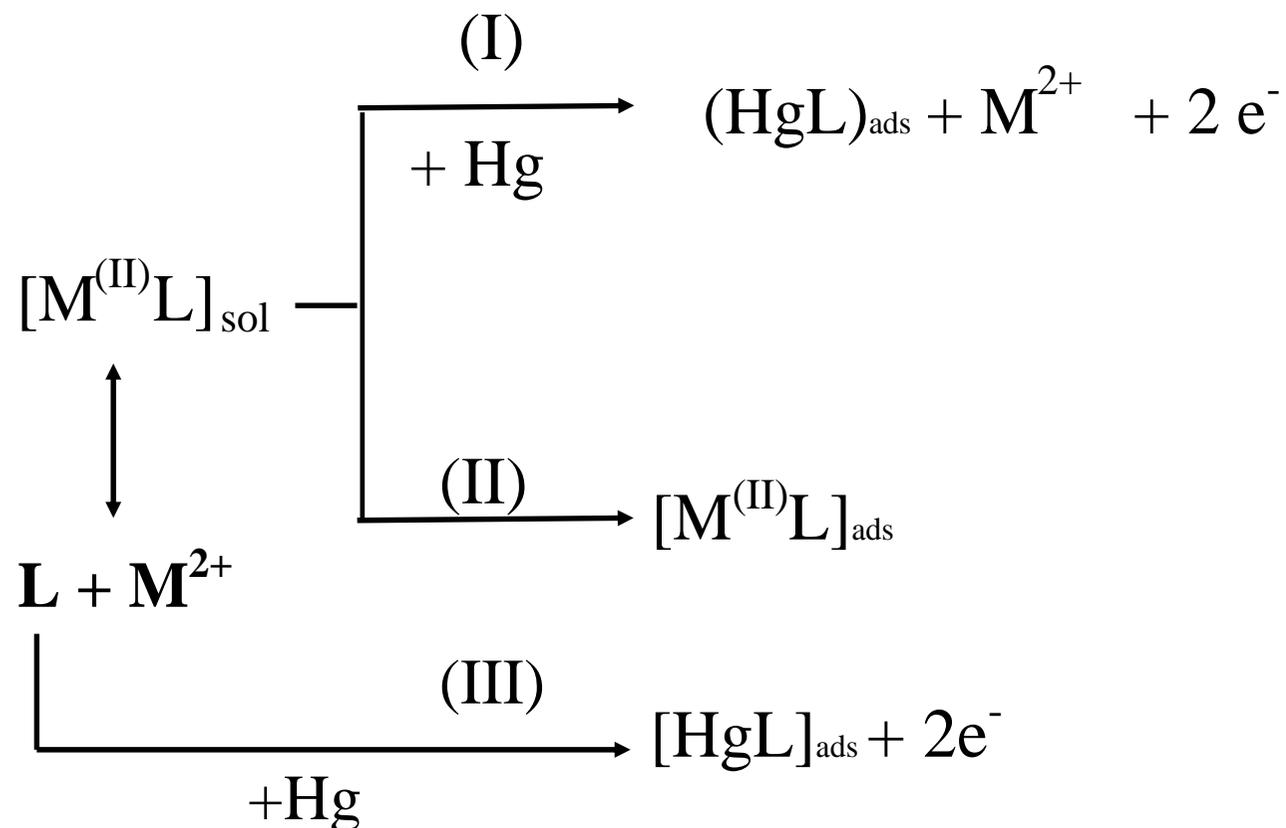
6-Mercaptopurine riboside (MPR)

### 3. Metal-ion catalytic reduction at the HMDE. Mechanism



## 4. Amino-thiols: pre-concentration mechanism

Analyte (L) state: complex form (high excess of  $M^{2+}$ )

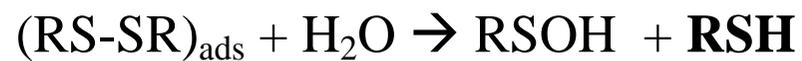


**Scheme 1**

## 5. Disulfides: pre-concentration mechanism

Two steps mechanism:

**Step 1: Mercury assisted hydrolysis followed by disproportionation:**



### ***Scheme 2***

**Step 2: RSH enter path I or II in Scheme 1**

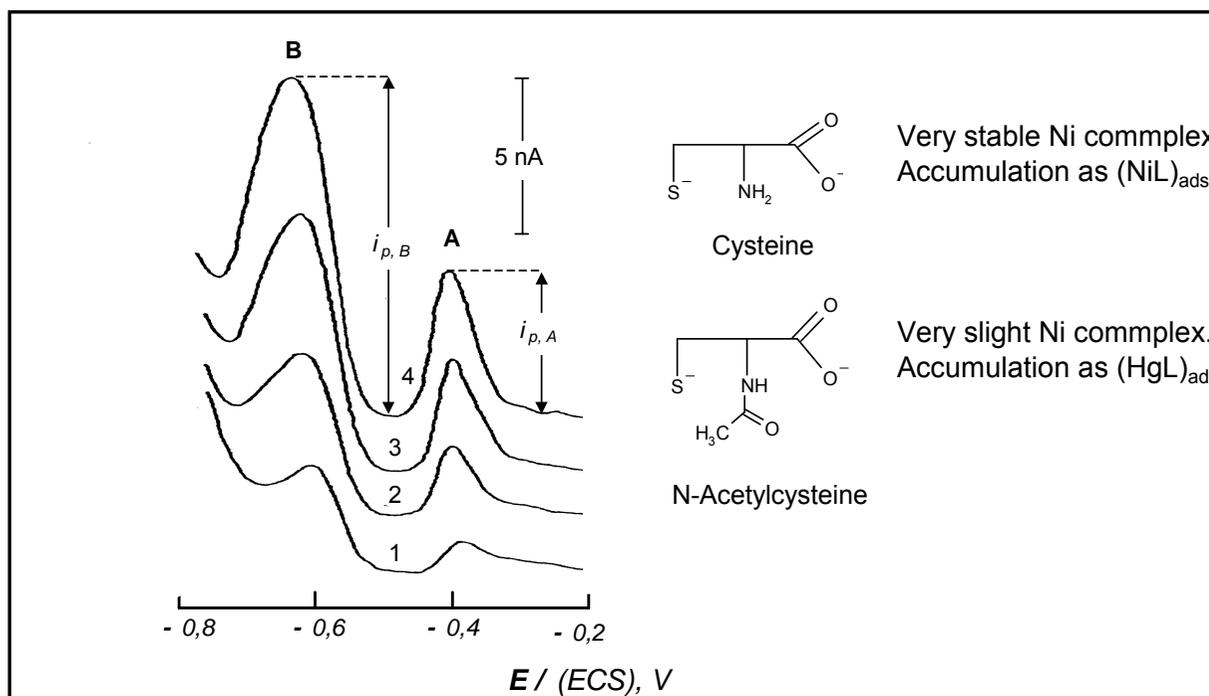
## 6. Effect of the deposition potential ( $E_d$ ) and [ML] stability on the pre-concentration pathway.

$E_{HgL}$  = electrode potential for mercury ion reduction in  $(HgL)_{ads}$

[ML] stability	<i>Very high</i> (CySH)	<i>Moderate</i> (GSH)	<i>Very low</i> (Ac-Cys)
$E_d > E_{HgL}$	Path I	Path I	Path III
$E_d < E_{HgL}$	Path II	No accumulation	No accumulation

## 7. Simultaneous determination of Cys and Ac-Cys by CSV in the presence of Ni<sup>2+</sup>

Cys determination by the catalytic peak B. Ac-Cys determination by Hg(II) reduction in the ([HgL]<sub>ads</sub> – (peak A)



**Experimental conditions:** pH 7; Ni(II) 0.5 mM. Accumulation: 2 min at -0.2 V(SCE). Cathodic scan by DPP. Curve 1: synthetic sample (**20 nM Cys; 10 nM Ac-Cys**). Curves 2 - 4: added 20, 40, 60 nM Cys and 15, 35, 55 nM Ac-Cys, respectively. **Found:** 22 nM Cys; 11 nM Ac-Cys.

## CONCLUSIONS

Stripping voltammetry of non-metallic analytes relies on two detection procedures: (1) tensammetric detection after adsorptive pre-concentration or (2) reduction of a metal ion (Hg, Cu) in a complex compound or a salt including the analyte. The last version belongs to the class of methods termed as indirect cathodic stripping voltammetry (A. G. Fogg, *Anal. Proc.*, 31, (1994) 313).

Detection by a catalytic electrode process forms an additional procedure for the detection of non-metallic compounds, either organic or inorganic. The signal appears at a characteristic potential and can be the most convenient when another kind of electrochemical signals (if available) is disturbed by interferences. In some instances, the catalytic process may be the only method for the determination of a compound by stripping voltammetry.

The catalytic activity of the analyte may depend on some subtle structure details and allows achieving a better selectivity. In addition to the catalytic effects, metal ions as  $\text{Ni}^{2+}$  or  $\text{Co}^{2+}$  may cause substantial modification in the behavior of the analyte during the pre-concentration step, as a consequence of complexation. Under these conditions, a proper selection of pre-concentration and stripping parameters permits an important improvement in selectivity.

The faradaic character of the catalytic detection makes the method less sensitive to the effect of some surface-active compounds. However, as is common in adsorptive stripping voltammetry, the disturbing effect of such compounds on the pre-concentration step cannot be always avoided.