

## INTRODUCTION

From the global amount of waste electric and electronic equipment (exceeding 50 Mt in 2018 [1]), the waste printed circuit boards (WPCBs) represent only 3-5% but concentrate more than 40% from the value of the recoverable metals [2]. Consequently, physico-mechanical, hydrometallurgical and pyrometallurgical techniques were designed for metals recovery from WPCBs (MRWPCBs), but all of them are energy intensive and/or highly polluting [3]. Our preliminary results [4] revealed that the electrochemical MRWPCBs represents an economical and eco-friendly recycling alternative if the operational parameters are well controlled.

## AIMS

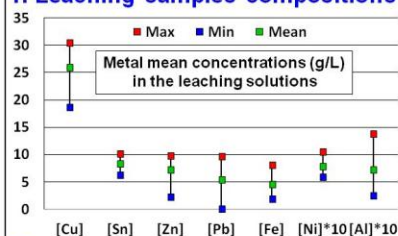
Design and validation of (i) a complex sensors system (amperometric, pH, temperature and ORP) able to assure the accurate monitoring and control of the MRWPCBs process and (ii) dedicated software applications for acquired data correlation.

## EXPERIMENTAL

- > **Real samples (RSs):** 10 PC mother boards (PCMBs) released between 1998 and 2008 were leached in 2.2 L of 2 M KBr + 0.5 M HBr + 1 M Br<sub>2</sub>. The resulting solutions were analyzed by ICP-AES and used for electrochemical measurements
- > **Synthetic samples (SSs):** Cu, Sn, Pb, Fe and Zn bromide salts in 2 M KBr + 0.5 M HBr.
- > **Electrochemical techniques:** cyclic (i) square wave & (ii) staircase voltammetry (CSWV & CV) @ 50 mV/s; potentiometric titration & pH measurement.
- > **Electrodes:** WE: glassy carbon (GC) disc ( $\phi = 3$  mm) for CSWV & CV; RE: Ag/AgCl/KCl<sub>SAT</sub>; CE & ORP-WE: Pt wire ( $\phi = 0.5$  mm, L = 10 cm).

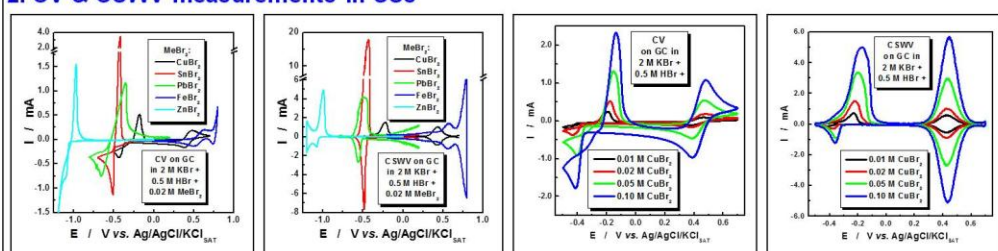
## RESULTS AND DISCUSSIONS

### 1. Leaching samples compositions



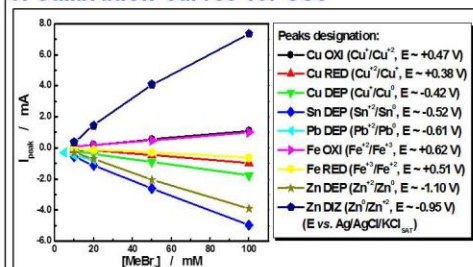
Depending on PCMBs type, the maximum and minimum concentrations of main metals vary between 20 and 100% in respect to the mean values

### 2. CV & CSWV measurements in SSs



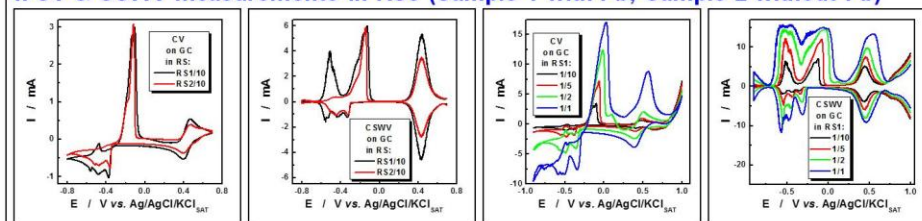
For the tested individual metals solutions, CV&CSWV reveal well defined electrodeposition (ELD) / dissolution (DIS) and/or reduction (RED) / oxidation (OXI) peaks useful for the concentrations monitoring.  
As exemplified for Cu, the ELD/DIS and/or RED/OXI peaks amplitudes evaluated for CV&CSWV present a good correlation with the concentration of the dissolved metal.

### 3. Calibration curves for SSs



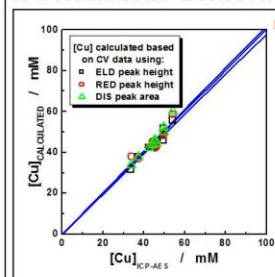
For Cu, Sn, Pb, Fe and Zn, the ELD, DIS, RED or OXI peaks amplitudes evaluated in SS by CV present excellent correlations with the concentrations of the dissolved metals.

### 4. CV & CSWV measurements in RSs (Sample 1 with Pb; Sample 2 without Pb)



The presence of Pb in RS1 determines the apparition of the corresponding distinctive DEP and DIS peaks, more evident in the CSWV measurements.  
Due to the complex composition and high metals ions concentrations in the undiluted RSs solutions, the ELD/DIS and/or RED/OXI peaks evaluated by CV&CSWV are obviously limited and distorted, requiring at least 10 times dilution for obtaining adequate analytical signals.

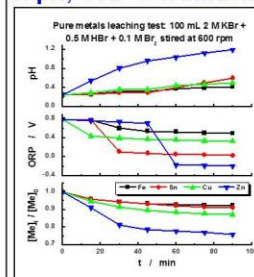
### 5. Correlations between ICP-AES and electrochemical data for RSs



Method	Slope	R	SD	N
ELD peak height	0.979 ± 0.013	0.9608	1.939	10
RED peak height	1.003 ± 0.019	0.9088	2.642	10
DIS peak area	1.017 ± 0.015	0.9706	2.085	10

As exemplified for the 10 RSs, the [Cu] values calculated using three CV data sets are in excellent agreement with those measured by ICP-AES.  
Similar correlations resulted for CSWV data.  
The accuracy of the CV&CSWV data can be improved restricting the voltage scan range and optimizing other experimental parameters.

### 6. pH, ORP & $\lambda$ influence on the metals leaching rates



The pH and ORP of the leaching solutions have a strong influence on the dissolution rate of metals.  
The pH and ORP sensors are essential for an adequate control and monitoring of the metals leaching process.  
Due to their high salinity and acidity, the leaching solutions conductivity is dimly affected by the dissolved metals concentrations.

## CONCLUSIONS

- ✓ In order to efficiently monitor and control the process of electrochemical metals recovery from waste printed circuit boards, a complex sensors system, based on pH, ORP, temperature and voltammetric sensors, was designed and the included components were successfully tested in synthetic and real samples using dedicated LabView applications.
- ✓ The simple and inexpensive amperometric sensors, exploited by CV or CSWV, allow the evaluation of the dissolved metals concentrations with satisfactory accuracy, eliminating the use of complex and expensive traditional analytical equipments and advanced dilutions.
- ✓ The electric signals delivered by the proposed sensors allow their integration in complex computerized and/or autonomous control systems, simplifying the metals recovery process management and increasing its efficiency.

## ACKNOWLEDGEMENT

This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI - UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0652 / 84PCCDI / 2018, within PNCDI III.

## REFERENCES

1. Z. Liu, J. Tang, B.-yi Li, Z. Wang, J. Clean. Prod., 2018, 167, 97-109.
2. F. Cuciurella, I. D'Adamo, S.C. Lenny Koh, P. Rosa, Renew. Sust. Energ. Rev. 2016, 64, 749-760.
3. C. Ning, C. S. K. Lin, D. C. W. Hui, G. McKay, Top. Curr. Chem., 2016, 375(2), 1-36.
4. S. A. Dorneanu, Studia UBB Chemia, 2017, LXII(3), 177-186.