

# Membrane electrolysis for recovering Sb and Bi from elution solutions of ion-exchange resins used in copper electrorefining: a cyclic voltammetric study

## SUPPLEMENTARY MATERIAL

Kayo Santana Barros <sup>1,2,3\*</sup>; André Luiz Vargas Machado <sup>1</sup>;  
Vicente Schaeffer Vielmo <sup>1</sup>; Svetlozar Velizarov <sup>3</sup>; Jane Zoppas Ferreira <sup>1</sup>;  
Valentín Pérez-Herranz <sup>2</sup>; Andréa Moura Bernardes <sup>1</sup>

<sup>1</sup> Post-Graduation Program in Mining, Metallurgical and Materials Engineering (PPGE3M), Federal University of Rio Grande do Sul (UFRGS), Av. Bento Gonçalves, 9500, 91501-970, Porto Alegre, Brazil.

<sup>2</sup> IEC Group, ISIRYM, Universitat Politècnica de València – Spain. Address: Camí de Vera s/n, 46022, P.O. Box 22012, València E-46071, Spain

<sup>3</sup> Associated Laboratory for Green Chemistry-Clean Technologies and Processes (LAQV), REQUIMTE, Chemistry Department, FCT NOVA, Universidade Nova de Lisboa, Caparica 2829-516, Portugal

\*Corresponding author: [kayo.barros@fct.unl.pt](mailto:kayo.barros@fct.unl.pt)

This supplementary material presents

- 1) speciation diagrams constructed for the solutions of Sb+HCl, Bi+HCl and Sb+Bi+HCl in different concentrations of Sb and Bi (Figure S1), concentrations of HCl (Figure S2), dilution factors (Figure S3), and with Fe<sup>3+</sup> ions as a contaminant (Figure S4). The diagrams were constructed with the aid of Hydra Medusa software [1] using equilibrium constants data present in ref. [2].
- 2) charge values of the cathodic ( $Q_c$ ) and anodic ( $Q_a$ ) peaks of Sb and Bi present in the solutions at different metals concentration (Table S1), HCl concentration (Table S2), dilution factors (Table S3), temperatures (Table S4), thiourea concentration (Table S5), and with Fe<sup>3+</sup> ions as a contaminant (Table S6).

Figure S1 shows the influence of increasing the concentration of (a) Sb, (b) Bi, (c) Sb and Bi on the species formed in each of the tested solutions. The figures were obtained by constructing speciation diagrams ( $\log [C]$  vs. pH) for Sb+HCl, Bi+HCl and Sb+Bi+HCl solutions using the following concentrations:

Figure S1(a):

0.25 g/L Sb + 6 M HCl;  
0.50 g/L Sb + 6 M HCl;  
0.75 g/L Sb + 6 M HCl;  
1.0 g/L Sb + 6 M HCl;  
1.5 g/L Sb + 6 M HCl;  
2.0 g/L Sb + 6 M HCl;  
4.0 g/L Sb + 6 M HCl.

Figure S1(b):

0.025 g/L Bi + 6 M HCl;  
0.05 g/L Bi + 6 M HCl;  
0.075 g/L Bi + 6 M HCl;  
0.1 g/L Bi + 6 M HCl;  
0.15 g/L Bi + 6 M HCl;  
0.2 g/L Bi + 6 M HCl;  
0.4 g/L Bi + 6 M HCl.

Figure S1(c):

0.25 g/L Sb + 0.025 g/L Bi + 6 M HCl;  
0.5 g/L Sb + 0.05 g/L Bi + 6 M HCl;  
0.75 g/L Sb + 0.075 g/L Bi + 6 M HCl;  
1.0 g/L Sb + 0.1 g/L Bi + 6 M HCl;  
1.5 g/L Sb + 0.15 g/L Bi + 6 M HCl;  
2.0 g/L Sb + 0.2 g/L Bi + 6 M HCl;  
4.0 g/L Sb + 0.4 g/L Bi + 6 M HCl.

From the diagrams obtained, the predominant species present in each solution at pH 0 were determined for constructing Figure S1, which shows  $\log [C]$  of the species in each of the solutions as a function of the concentration of metals.

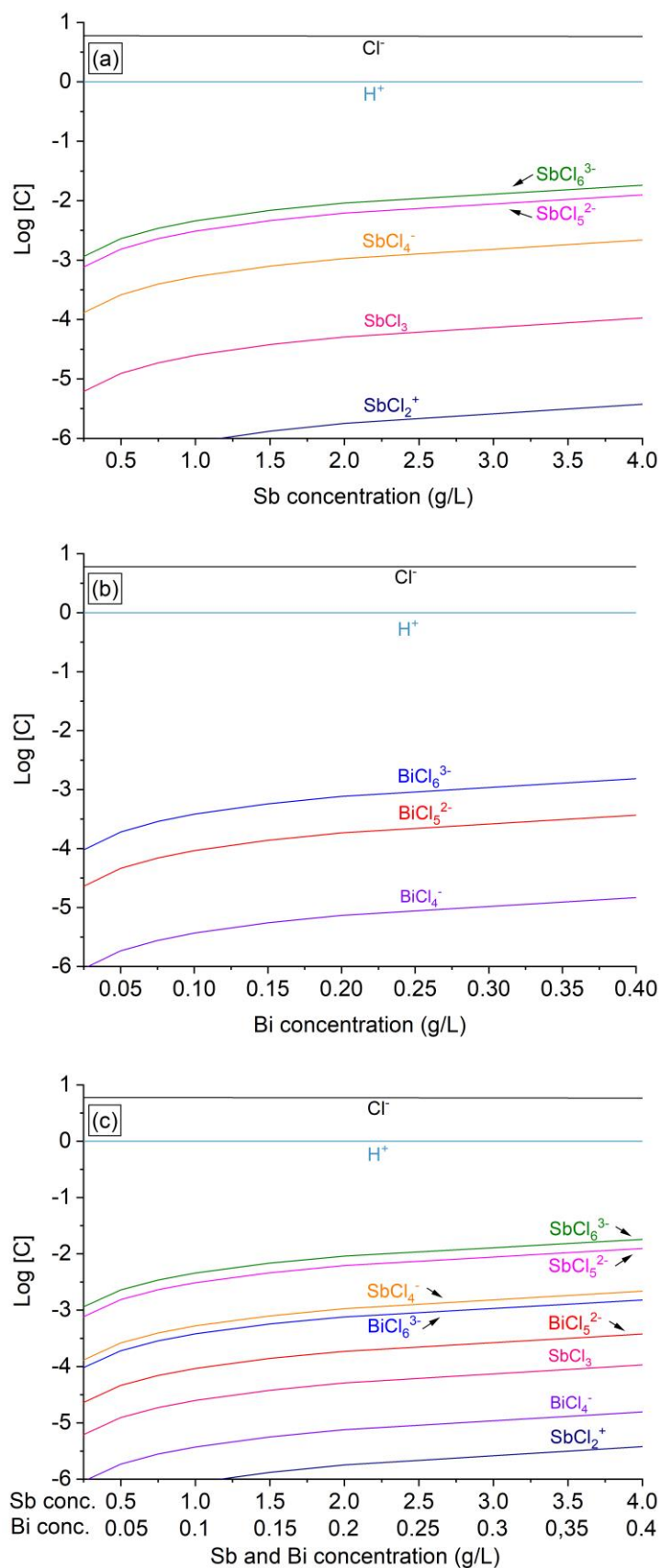


Figure S1 – Speciation diagram constructed for the solution of (a) Sb (0.25 g/L – 4 g/L) + HCl (6 M), (b) Bi (0.025 g/L – 0.4 g/L) + HCl (6 M), and (c) Sb (0.25 g/L – 4 g/L) + Bi (0.025 g/L – 0.4 g/L) + HCl (6 M).

Figure S2 shows the influence of increasing the concentration of HCl (4 M – 7 M) in the solutions with (a) Sb, (b) Bi, (c) Sb and Bi on the species formed in each of the tested solutions. The figures were obtained by constructing speciation diagrams ( $\log [C]$  vs. pH) for Sb+HCl, Bi+HCl and Sb+Bi+HCl solutions using the following concentrations:

Figure S2(a):

1.0 g/L Sb + 4 M HCl;  
1.0 g/L Sb + 5 M HCl;  
1.0 g/L Sb + 6 M HCl;  
1.0 g/L Sb + 7 M HCl.

Figure S2(b):

0.1 g/L Bi + 4 M HCl;  
0.1 g/L Bi + 5 M HCl;  
0.1 g/L Bi + 6 M HCl;  
0.1 g/L Bi + 7 M HCl.

Figure S2(c):

1.0 g/L Sb + 0.1 g/L Bi + 4 M HCl;  
1.0 g/L Sb + 0.1 g/L Bi + 5 M HCl;  
1.0 g/L Sb + 0.1 g/L Bi + 6 M HCl;  
1.0 g/L Sb + 0.1 g/L Bi + 7 M HCl.

From the diagrams obtained, the predominant species present in each solution at pH 0 were determined for constructing Figure S2, which shows  $\log [C]$  of the species in each of the solutions as a function of the concentration of HCl.

It is worth mentioning that the concentration of  $H^+$  ions in the diagrams is constant with increasing concentration of HCl. This occurred because for the construction of Figure S2, the concentrations of the predominant species in solution were determined for the same pH value (zero) of the curves. Therefore, in a real system, one must consider the increase in  $H^+$  concentration, which is not shown in Figure S2.

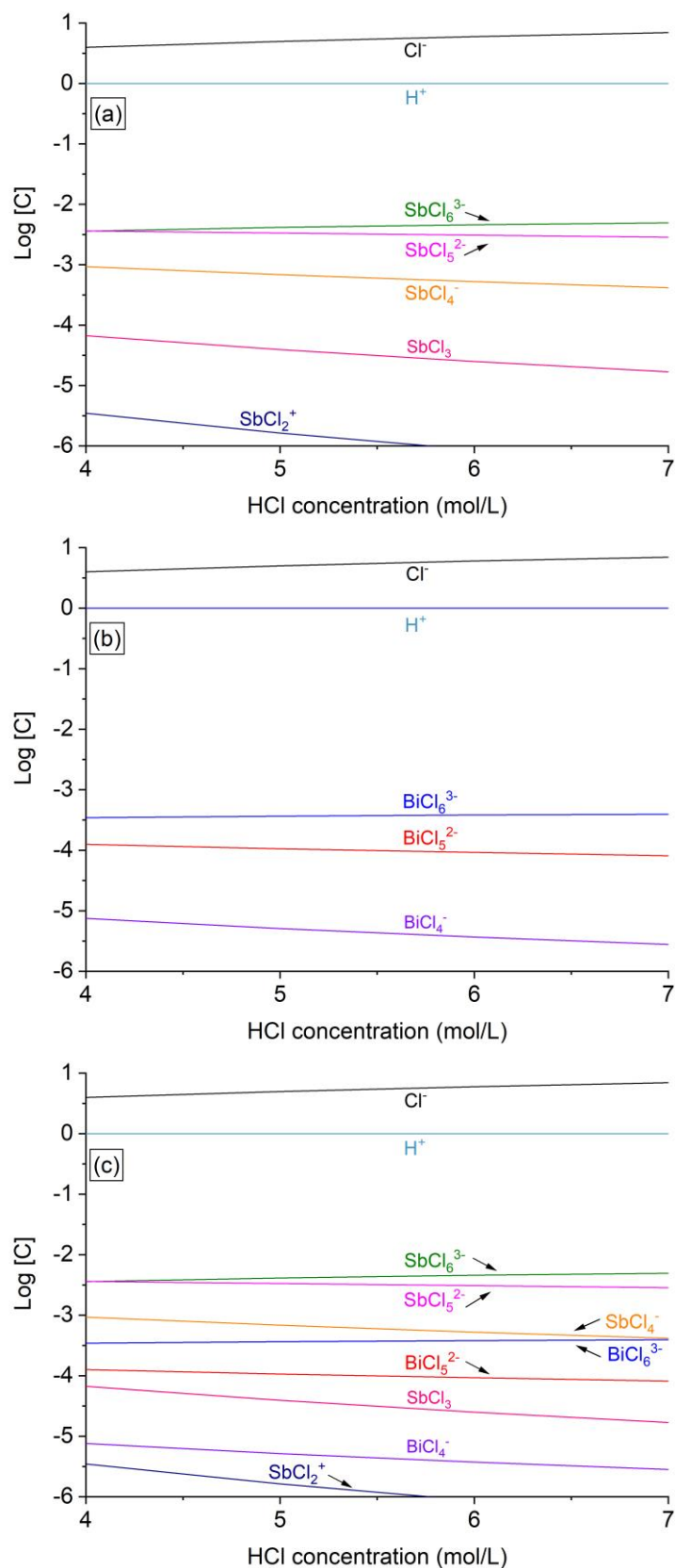


Figure S2 - Speciation diagram constructed for the solution of (a) Sb (1 g/L) + HCl (4 M - 7 M), (b) Bi (0.1 g/L) + HCl (4 M - 7 M), and (c) Sb (1 g/L) + Bi (0.1 g/L) + HCl (4 M - 7 M).

Figure S3 shows the influence of diluting the solutions of (a) Sb+HCl, (b) Bi+HCl, (c) Sb+Bi+HCl on the species formed in each of the tested solutions. Solutions presenting 35%, 50% and 75% of Sb, Bi and HCl concentration in the original solution (100%) were considered. The figures were obtained by constructing speciation diagrams (log [C] vs. pH) for Sb+HCl, Bi+HCl and Sb+Bi+HCl solutions using the following concentrations:

Figure S3(a):

0.35 g/L Sb + 2.1 M HCl;

0.5 g/L Sb + 3 M HCl;

0.75 g/L Sb + 4.5 M HCl;

1.0 g/L Sb + 6 M HCl.

Figure S3(b):

0.035 g/L Bi + 2.1 M HCl;

0.05 g/L Bi + 3 M HCl;

0.075 g/L Bi + 4.5 M HCl;

0.1 g/L Bi + 6 M HCl.

Figure S3(c):

0.35 g/L Sb + 0.035 g/L Bi + 2.1 M HCl;

0.5 g/L Sb + 0.05 g/L Bi + 3 M HCl;

0.75 g/L Sb + 0.075 g/L Bi + 4.5 M HCl;

1.0 g/L Sb + 0.1 g/L Bi + 6 M HCl.

From the diagrams obtained, the predominant species present in each solution at pH 0 were determined for constructing Figure S3, which shows log [C] of the species in each of the solutions as a function of the percentage of Sb, Bi and HCl concentration in relation to the original solution (100%).

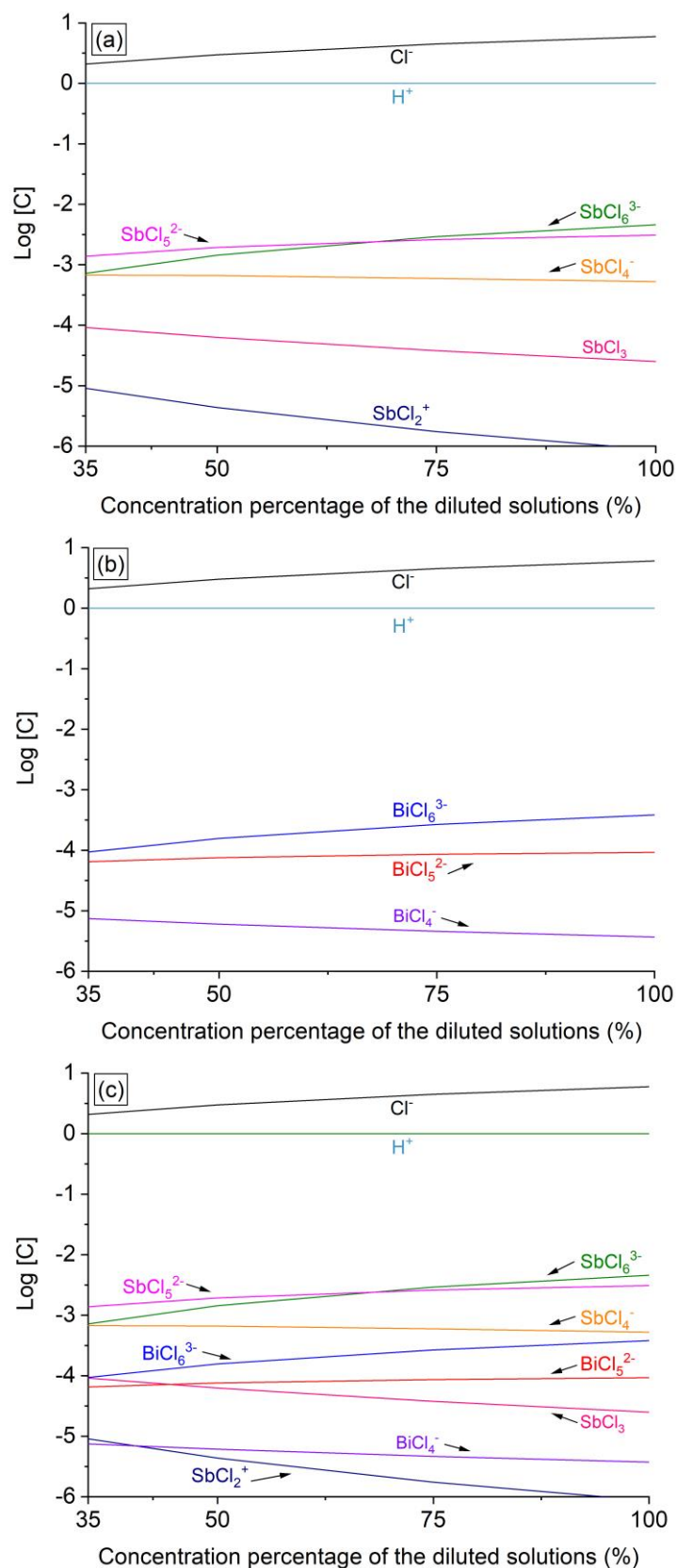


Figure S3 - Speciation diagram constructed for the diluted solution of (a) Sb + HCl, (b) Bi + HCl, and (c) Sb + Bi + HCl presenting 35%, 50% and 75% of Sb, Bi and HCl concentration in relation to the original solution (100%).

Figure S4 shows the influence of the presence of Fe in the solutions with (a) Sb, (b) Bi, (c) Sb and Bi on the species formed in each of the tested solutions. The figures were obtained by constructing speciation diagrams ( $\log [C]$  vs. pH) for Sb+HCl+Fe, Bi+HCl+Fe, and Sb+Bi+HCl+Fe solutions using the following concentrations:

Figure S4(a): 1.0 g/L Sb + 6.0 M HCl + 0.1 g/L Fe<sup>3+</sup>;

Figure S4(b): 0.1 g/L Bi + 6.0 M HCl + 0.1 g/L Fe<sup>3+</sup>;

Figure S4(c): 1.0 g/L Sb + 0.1 g/L Bi + 6.0 M HCl + 0.1 g/L Fe<sup>3+</sup>.

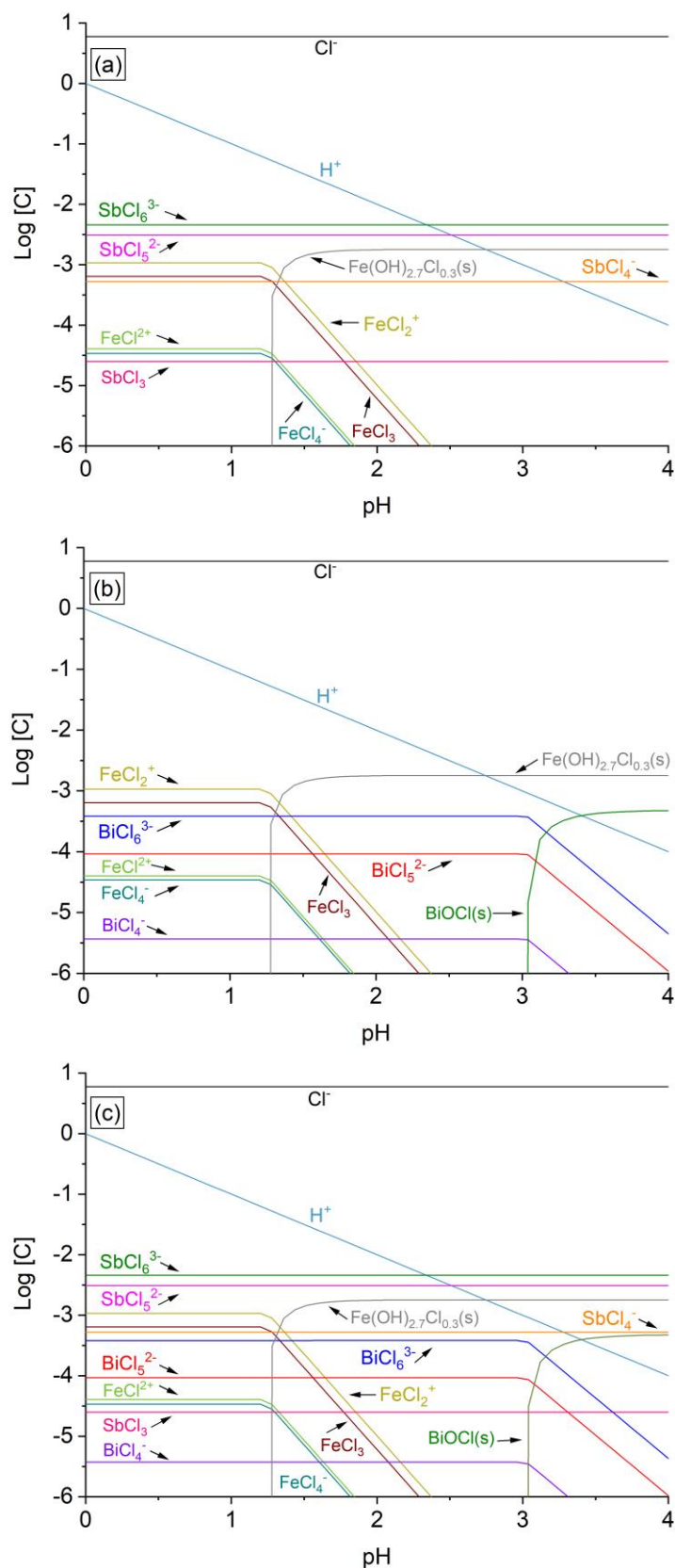


Figure S4 - Speciation diagram constructed for the solution of (a) Sb (1 g/L) + HCl (6 M) +  $\text{Fe}^{3+}$  (0.1 g/L), (b) Bi (0.1 g/L) + HCl (6 M) +  $\text{Fe}^{3+}$  (0.1 g/L), and (c) Sb (1 g/L) + Bi (0.1 g/L) + HCl (6 M) +  $\text{Fe}^{3+}$  (0.1 g/L).

Table S1 - Charge of the cathodic ( $Q_c$ ) and anodic ( $Q_a$ ) peaks of Sb and Bi present at different concentrations in the HCl solutions, which are shown in Figure 6.

Solution of Sb+HCl			
Concentration (g/L)	$Q_a$ ( $C/cm^2$ )	$Q_c$ ( $C/cm^2$ )	$Q_a/Q_c$
0.25	0.009	0.009	1.1
0.50	0.017	0.014	1.2
0.75	0.027	0.021	1.3
1.0	0.033	0.026	1.3
1.5	0.155	0.036	4.3
2.0	0.594	0.041	14.5
4.0	1.597	0.088	18.2
Solution of Bi+HCl			
Concentration (g/L)	$Q_a$ ( $C/cm^2$ )	$Q_c$ ( $C/cm^2$ )	$Q_a/Q_c$
0.025	0.004	0.001	2.8
0.05	0.005	0.002	3.3
0.075	0.009	0.003	3.0
0.1	0.011	0.003	3.2
0.15	0.016	0.004	3.7
0.2	0.022	0.005	4.2
0.4	0.042	0.008	5.1
Solution of Sb+Bi+HCl			
Concentration (g/L)	$Q_a$ ( $C/cm^2$ )	$Q_c$ ( $C/cm^2$ )	$Q_a/Q_c$
0.25 (Sb) + 0.025 (Bi)	0.064	0.012	5.4
0.50 (Sb) + 0.05 (Bi)	0.094	0.012	7.7
0.75 (Sb) + 0.075 (Bi)	0.170	0.019	8.9
1.0 (Sb) + 0.1 (Bi)	0.315	0.022	14.1
1.5 (Sb) + 0.15 (Bi)	0.479	0.035	13.8
2.0 (Sb) + 0.2 (Bi)	0.729	0.042	17.3
4.0 (Sb) + 0.4 (Bi)	1.697	0.088	19.3

Table S2 - Charge of the cathodic ( $Q_c$ ) and anodic ( $Q_a$ ) peaks of Sb and Bi present in the solutions with HCl at different concentrations, which are shown in Figure 7.

Solution of Sb+HCl			
HCl concentration (mol/L)	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
4	0.088	0.031	2.8
5	0.058	0.031	1.9
6	0.033	0.026	1.3
7	0.032	0.025	1.3
Solution of Bi+HCl			
HCl concentration (mol/L)	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
4	0.010	0.003	3.6
5	0.009	0.003	3.0
6	0.011	0.003	3.2
7	0.011	0.005	2.2
Solution of Sb+Bi+HCl			
HCl concentration (mol/L)	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
4	0.264	0.026	10.2
5	0.278	0.023	12.2
6	0.315	0.022	14.1
7	0.374	0.021	17.4

Table S3 - Charge of the cathodic ( $Q_c$ ) and anodic ( $Q_a$ ) peaks of Sb and Bi present in the HCl solutions prepared with different dilution factors, which are shown in Figure 8.

Solution of Sb+HCl			
Percentage of Sb, Bi and HCl concentration in relation to the original solution (100%)	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
35%	0.013	0.013	1.0
50%	0.027	0.017	1.4
75%	0.030	0.023	1.3
100%	0.033	0.026	1.3
Solution of Bi+HCl			
Percentage of Sb, Bi and HCl concentration in relation to the original solution (100%)	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
35%	0.005	0.002	3.4
50%	0.006	0.002	3.4
75%	0.009	0.003	3.4
100%	0.011	0.003	3.2
Solution of Sb+Bi+HCl			
Percentage of Sb, Bi and HCl concentration in relation to the original solution (100%)	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
35%	0.064	0.014	4.5
50%	0.090	0.017	5.5
75%	0.179	0.021	8.7
100%	0.315	0.022	14.1

Table S4 - Charge of the cathodic ( $Q_c$ ) and anodic ( $Q_a$ ) peaks of Sb and Bi present in HCl solutions at different temperatures, which are shown in Figure 9.

Solution of Sb+HCl			
Temperature (°C)	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
20	0.033	0.025	1.3
30	0.057	0.024	2.4
40	0.089	0.027	3.2
50	0.153	0.028	5.5
Solution of Bi+HCl			
Temperature (°C)	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
20	0.003	0.003	1.0
30	0.004	0.004	1.1
40	0.005	0.004	1.2
50	0.012	0.006	2.1
Solution of Sb+Bi+HCl			
Temperature (°C)	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
20	0.090	0.021	4.4
30	0.165	0.024	6.9
40	0.243	0.023	10.4
50	0.311	0.024	12.9

Table S5 - Charge of the cathodic ( $Q_c$ ) and anodic ( $Q_a$ ) peaks of Sb and Bi present in HCl solutions with thiourea at different concentrations, which are shown in Figure 11.

Solution of Sb+HCl+thiourea			
Sb/thiourea molar ratio	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
0	0.033	0.026	1.3
0.5	0.030	0.021	1.4
1	0.044	0.020	2.2
2	0.063	0.021	3.0
3	0.059	0.019	3.1
Solution of Bi+HCl+thiourea			
Sb/thiourea molar ratio	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
0	0.011	0.003	3.2
0.5	0.010	0.003	3.0
1	0.010	0.004	2.8
2	0.010	0.004	2.6
3	0.010	0.004	2.7
Solution of Sb+Bi+HCl+thiourea			
Sb/thiourea molar ratio	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
0	0.315	0.022	14.1
0.5	0.287	0.017	17.1
1	0.282	0.016	17.6
2	0.297	0.016	18.56
3	0.281	0.014	20.59

Table S6 - Charge of the cathodic ( $Q_c$ ) and anodic ( $Q_a$ ) peaks of Sb and Bi present in HCl solutions with Fe<sup>3+</sup> ions, which are shown in Figure 12.

Solution of Sb+HCl+Fe			
Fe <sup>3+</sup> concentration (g/L)	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
0	0.033	0.026	1.3
0.1	0.027	0.027	1.0
Solution of Bi+HCl+Fe			
Fe <sup>3+</sup> concentration (g/L)	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
0	0.011	0.003	3.2
0.1	0.010	0.005	2.2
Solution of Sb+Bi+HCl+Fe			
Fe <sup>3+</sup> concentration (g/L)	$Q_a$ (C/cm <sup>2</sup> )	$Q_c$ (C/cm <sup>2</sup> )	$Q_a/Q_c$
0	0.315	0.022	14.1
0.1	0.306	0.023	13.1

## References

- [1] I. Puigdomench, Hydra Medusa — Make Equilibrium Diagrams using Sophisticated Algorithms, (2001).
- [2] P.M. Vereecken, S. Ren, L. Sun, P.C. Searson, Electrodeposition of Bi<sub>1-x</sub>Sb<sub>x</sub> Thin Films, J. Electrochem. Soc. 150 (2003) C131. doi:10.1149/1.1545458.