SUPPLEMENTARY MATERIAL

Chemometric-assisted electrochemical sensor for simultaneous determination of neonicotinoids imidacloprid and thiamethoxam in honey samples

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Communication to: Analytical Methods

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Table S1. Concentration values of IM and TM in honey diluted 10% with pH 8 PBS used as output data in the calibration set (samples 1–11) and the validation set (samples 12–21).

Experience	c^*_{TM} / **mg L^{-1}**	c^*_{IM} / **mg L^{-1}**
1	5.5	22.0
2	29.0	13.4
3	15.3	13.4
4	25	4.8
5	15.3	1.3
6	5.5	4.8
7	15.3	13.4
8	15.3	25.0
9	25	22
10	15.3	13.4
11	1.4	13.4
12	22.5	19.7
13	26.3	11.8
14	13.4	11.8
15	13.4	0.5
16	4.3	3.8
17	13.4	11.8
18	13.4	23.0
19	4.3	19.7
20	0.6	11.8
21	22.5	3.8

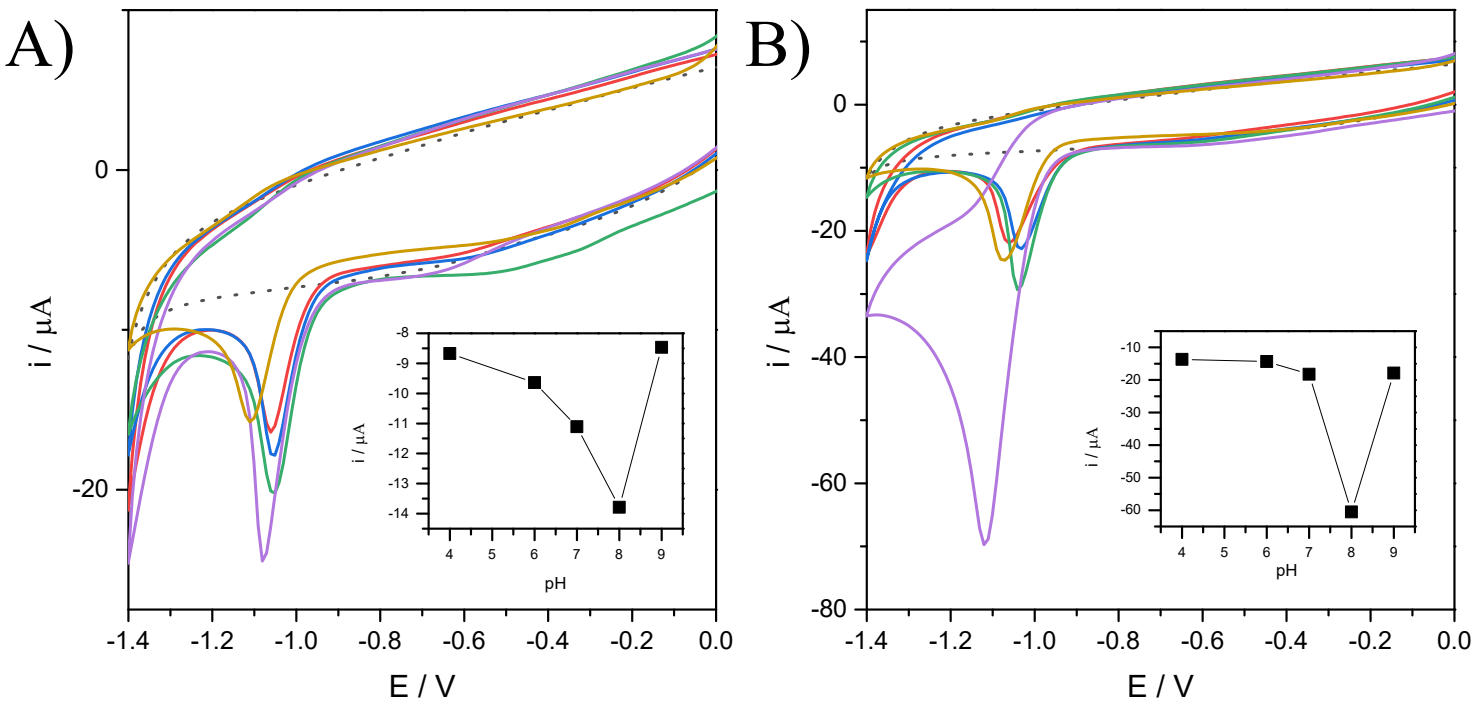

Figure S1. Cyclic voltammograms obtained for A) TM 1x10^{-4} mol L^{-1} and B) IM 1x10^{-4} mol L^{-1} at 50 mV s^{-1} in pH 8 PBS. Insert: Dependence between the reduction peak currents and the pH.

Table S2. Five-factor central composite design and corresponding responses.

		Factors					Responses	
Experiments	Block	pH	Frequency of the SWV / Hz	Amplitude of the SWV / mV	Staircase potential of the SWV / mV	GCE activation cycles	Area / µA V	*Ip* / µA
31	1	4	30	35	7	2	3.25	18.7
1	2	5	40	45	9	1	2.06	13.6
4	2	5	40	45	5	1	0.23	1.4
5	2	5	20	25	5	1	0.75	5
10	2	5	20	25	5	3	0.63	3.6
11	2	5	40	25	5	3	2.63	20.6
12	2	5	20	45	5	3	1.03	6.09
19	2	5	20	45	5	1	1.56	10.8
22	2	5	20	25	9	1	2.67	20.5
23	2	5	40	25	9	3	2.3	15.8
26	2	5	40	45	9	3	2.23	15.7
32	2	5	20	45	9	1	2.21	16.1
33	2	5	40	25	9	1	2.79	20.3
36	2	5	20	45	9	3	1.83	11.8
38	2	5	40	25	5	1	0.97	6.6
40	2	5	20	25	9	3	2.94	22.5
44	2	5	40	45	5	3	1.13	1.09
2	3	7	30	35	7	2	0.19	2.55
3	3	7	30	35	7	1	2.5	19.4
6	3	7	30	50	7	2	3.8	27.6
7	3	7	30	35	7	2	3.5	26
9	3	7	30	35	10	2	3.71	28.8
16	3	7	45	35	7	2	4.22	31.4
20	3	7	30	35	4	2	1.77	14.8
25	3	7	15	35	7	2	2.36	17.6

30	3	7	30	20	7	2	0.21	1.9
34	3	7	30	35	7	2	2.75	23.1
42	3	7	30	35	7	3	2.91	21.4
13	4	9	40	25	5	3	1.43	10.2
14	4	9	40	25	9	1	3.27	20.8
15	4	9	20	25	9	1	2.36	17.8
17	4	9	20	45	9	3	3.64	21.9
18	4	9	40	25	9	3	3.3	21.3
21	4	9	40	25	5	1	0.64	4.7
24	4	9	40	45	9	3	1.07	15.4
27	4	9	40	45	9	1	6.46	36.9
28	4	9	20	45	5	1	2.53	17.7
29	4	9	20	45	9	1	4.33	25.6
35	4	9	40	45	5	1	3.18	21.4
37	4	9	20	25	5	1	1.42	10.6
39	4	9	20	45	5	3	2.04	13.7
41	4	9	20	25	9	3	3.3	25.2
43	4	9	20	25	5	3	1.79	11.4
45	4	9	40	45	5	3	4.89	28.7
8	5	10	30	35	7	2	2.24	19.6

Table S3. ANOVA obtained when a central composite design was applied for the optimization of IM and TM response in terms of area and Ip.

ANOVA for Response Surface Reduced 2FI model						
Analysis of variance table [Response 1: Area]						
	Sum of		**Mean**	**F**	**p-value**	
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**	
Model	33.07	6	5.51	4.94	0.0008	significant
A-pH	*7.17*	*1*	*7.17*	*6.42*	*0.0155*	
B- Frequency of the SWV	*1.10*	*1*	*1.10*	*0.99*	*0.3270*	
C- Amplitude of the SWV	*4.36*	*1*	*4.36*	*3.90*	*0.0555*	
D- Staircase potential of the SWV	*14.27*	*1*	*14.27*	*12.78*	*0.0010*	
E- GCE activation cycles	*0.021*	*1*	*0.021*	*0.019*	*0.8923*	
AC	*6.15*	*1*	*6.15*	*5.51*	*0.0242*	
Residual	42.44	38	1.12			
Lack of Fit	*36.41*	*36*	*1.01*	*0.34*	*0.9364*	*not significant*
Pure Error	*6.02*	*2*	*3.01*			
Cor Total	75.51	44				

ANOVA for Response Surface Reduced 2FI model						
Analysis of variance table [Response 1: Ip]						
	Sum of		**Mean**	**F**	**p-value**	
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**	
Model	1558.36	6	259.73	5.74	0.0003	significant
A-pH	*350.89*	*1*	*350.89*	*7.76*	*0.0083*	
B-Frequency of the SWV	*33.37*	*1*	*33.37*	*0.74*	*0.3957*	
C- Amplitude of the SWV	*97.09*	*1*	*97.09*	*2.15*	*0.1511*	
D- Staircase potential of the SWV	*778.98*	*1*	*778.98*	*17.23*	*0.0002*	
E- GCE activation cycles	*0.23*	*1*	*0.23*	*5.173E-003*	*0.9430*	
AC	*297.80*	*1*	*297.80*	*6.59*	*0.0143*	

Residual	1718.28	38	45.22			
Lack of Fit	*1391.41*	*36*	*38.65*	*0.24*	*0.9776*	*not significant*
Pure Error	*326.87*	*2*	*163.44*			
Cor Total	3276.64	44				

Table S4. Criteria used for the optimization.

Factors and response	Optimization criteria	Lower limit	Upper limit	Predicted SRO-ANN	Experimental values
pH	In range	5	9	8	
Amplitude of the SWV	In range	25	45	43	
Staircase potential of the SWV	In range	5	9	9	
Area	Maximize	0.2	6.4	3.7	4.1 ± 0.4
I_p	Maximize	1.1	36	26.3	27.4 ± 1.2

Table S5. Optimized parameters and errors obtained between nominal and estimated concentrations by ANNs.

	TM	IM
Architecture	3-5-1	3-5-1
Number of iterations	30	25

Hidden layer transfer function	Tansing	Tansing
RMSEP[a] (mol L^{-1})	$1.4x10^{-6}$	$2.9x10^{-6}$
REP[a] (%)	2.9	6.5
R^2	0.9984	0.9886

[a] Errors obtained between nominal and estimated concentrations by ANNs for the calibration set.

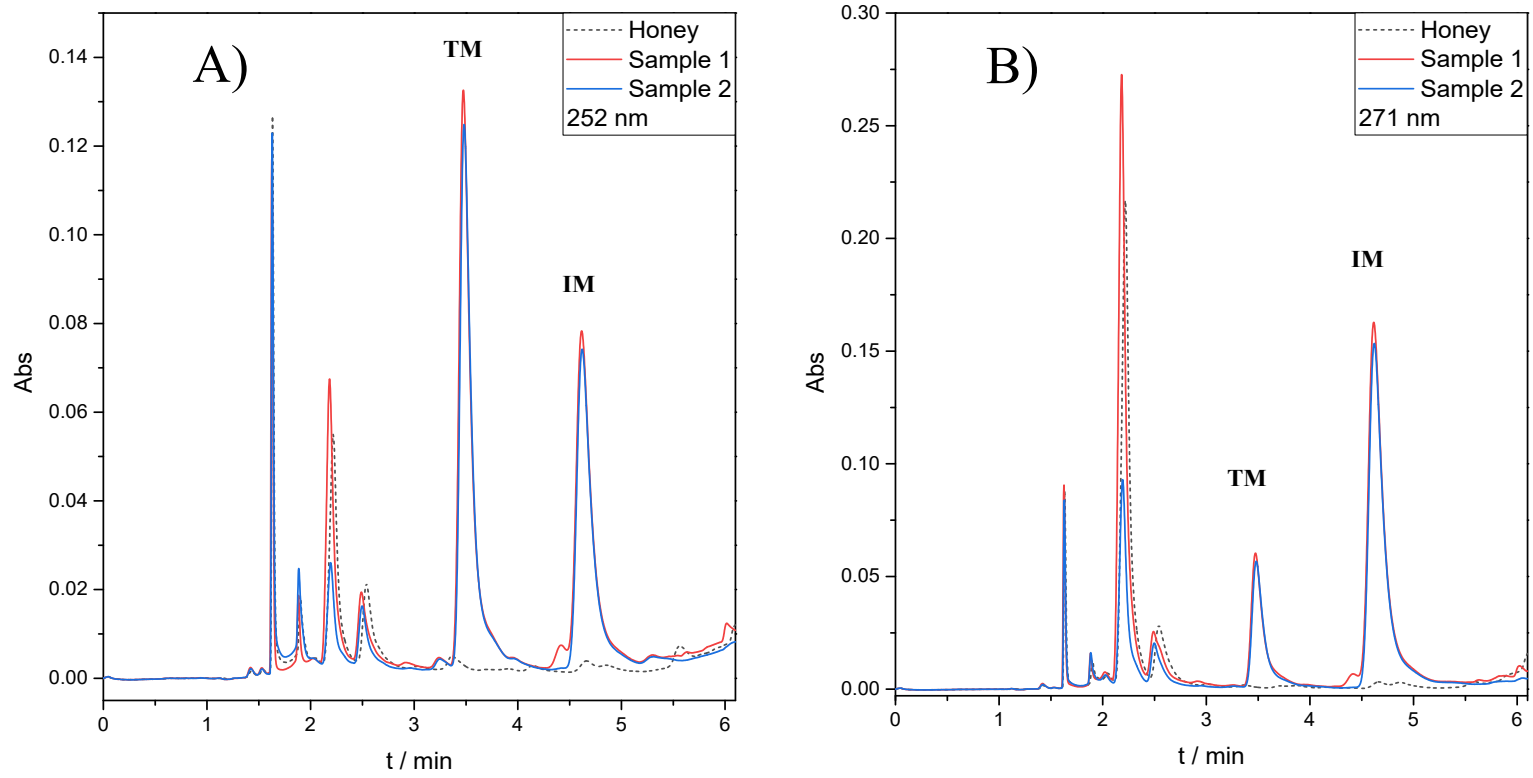

Figure S2. Chromatographic profile of honey samples (dotted black points) taken at A) 252 nm and B) 271 nm. Samples 1 and 2 are honey samples with addition of TM and IM at different concentration.

Data availability statements

The code for surface response modelling and desirability function calculations can be found at https://www.iquir-conicet.gov.ar/2022/10/03/quimiometria-analitica/ . The version of the code employed for this study is version [SRO_ANN MatLab toolbox].

The code for construction of the calibration model with ANN can be found at https://www.iquir-conicet.gov.ar/2022/10/03/quimiometria-analitica/ with [https://doi.org/10.1016/j.chemolab.2004.03.004]. The version of the code employed for this study is version [MVC1 package].

The code for Green analysis was can be found at https://mostwiedzy.pl/wojciech-wojnowski,174235-1/AGREE with [https://doi.org/10.1021/acs.analchem.0c01887]. The version of the code employed for this study is version [Analytical GREEnness Metric Approach and Software].