membranes

MDPI

Supporting Information

Integration of response surface methodology (RSM) and principal component analysis (PCA) as an optimization tool of polymer inclusion membrane based-optodes designed for Hg(II), Cd(II) and Pb(II)

Jeniffer García-Beleño, Eduardo Rodríguez de San Miguel*

Departamento de Química Analítica, Facultad de Química, Universidad Nacional Autónoma de México (UNAM), Ciudad Universitaria, 04510, Ciudad de México, México; jgarciab@comunidad.unam.mx

* Correspondence: erdsmg@unam.mx

Table S1. Values of the predicted desirability of the multivariate analysis performed with the M1 process method, using Dz as chromophore.

Experimental runs	Response		
	Expected Desirability		
	Dz – Hg(II)	Dz – Cd(II)	Dz – Pb(II)
1	0.587493	0.412899	0.583719
2	0.587493	0.412899	0.583719
3	0.47074	0.239581	0.0
4	0.557221	0.351363	0.494072
5	0.467964	0.384996	0.447025
6	0.587493	0.412899	0.583719
7	0.639942	0.614606	0.583512
8	0.61091	0.451523	0.580387
9	0.498601	0.550099	0.515556
10	0.639942	0.462867	0.476102
11	0.61091	0.469964	0.548087
12	0.705562	0.526763	0.444928
13	0.47074	0.180432	0.313694
14	0.519043	0.294723	0.535386
15	0.519043	0.242642	0.609567
16	0.557221	0.365713	0.482335
17	0.628188	0.504092	0.655115
18	0.587493	0.440114	0.583719
19	0.634034	0.364699	0.39621
20	0.628188	0.320985	0.799071
21	0.587493	0.383758	0.583719
22	0.587493	0.412899	0.583719

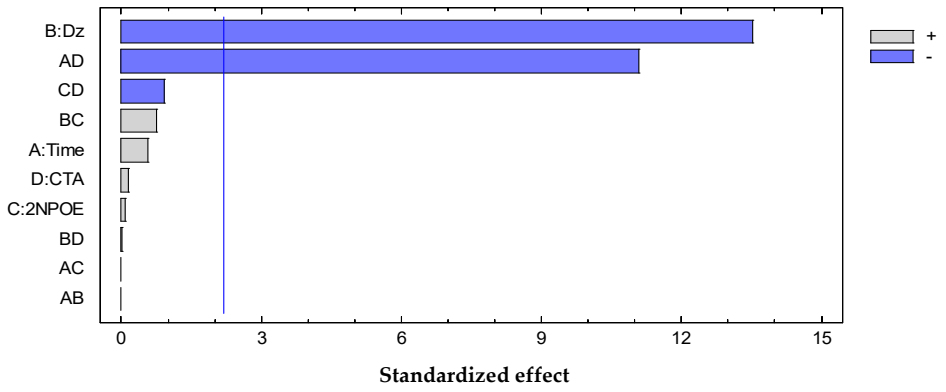


Figure S1. Pareto of the multivariate analysis performed with the M1 process method for the system Dz – Hg(II).

Table S2. ANOVA values of the multivariate analysis performed with the M1 process method for the system Dz – Hg(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,0000836037	1	0,0000836037	0,33	0,5759
B:Dz	0,0460006	1	0,0460006	182,85	**0,0000**
C:2NPOE	0,0000018768	1	0,0000018768	0,01	0,9327
D:CTA	0,00000643161	1	0,00000643161	0,03	0,8759
AB	0,0	1	0,0	0,00	1,0000
AC	0,0	1	0,0	0,00	1,0000
AD	0,0309215	1	0,0309215	122,91	**0,0000**
BC	0,0001458	1	0,0001458	0,58	0,4625
BD	1,26293E-7	1	1,26293E-7	0,00	0,9825
CD	0,000213563	1	0,000213563	0,85	0,3766
Total Error	0,00276736	11	0,000251578		
Total (corrected)	0,0840181	21			
R^2	96,7062 %				
Adj - R^2	93,7119 %				
Standard error	0,0158612				
Std. Dev	0,00881342				

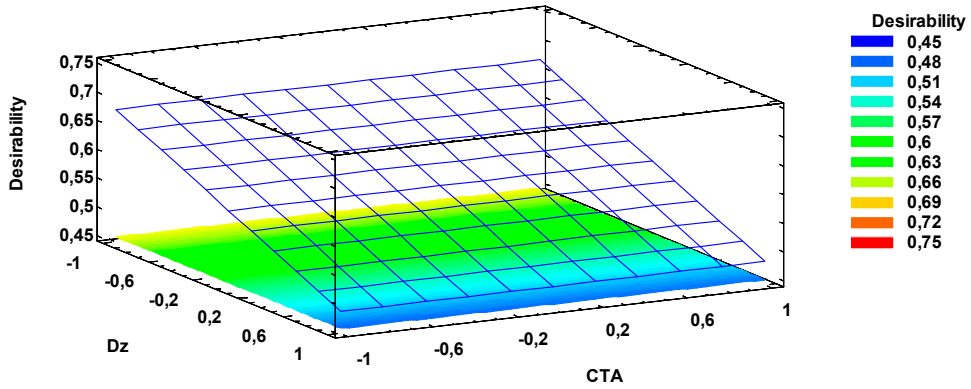


Figure S2. Response surface and contour plots of the multivariate analysis performed with the M1 process method for the system Dz – Hg(II), when 2NPOE = Time = 0,0.

For the Dz – Hg(II) system the model was:

D = 0.576507 - 0.09592*Dz - 0.235797*Time*CTA (S1)

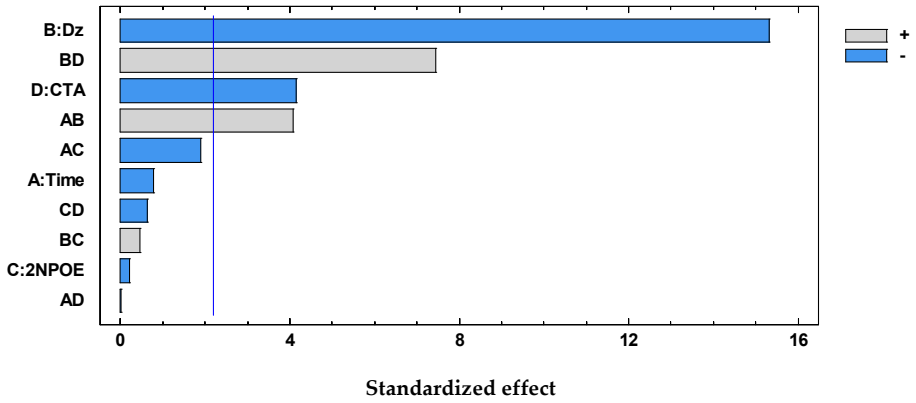


Figure S3. Pareto of the multivariate analysis performed with the M1 process method for the system Dz – Cd(II).

Table S3. ANOVA values of the multivariate analysis performed with the M1 process method for the system Dz – Cd(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,00041896	1	0,00041896	0,62	0,4469
B:Dz	0,158043	1	0,158043	234,68	**0,0000**
C:2NPOE	0,0000281747	1	0,0000281747	0,04	0,8417
D:CTA	0,0116151	1	0,0116151	17,25	**0,0016**
AB	0,0111184	1	0,0111184	16,51	**0,0019**
AC	0,00239427	1	0,00239427	3,56	0,0860
AD	2,15028E-7	1	2,15028E-7	0,00	0,9861
BC	0,00013992	1	0,00013992	0,21	0,6574
BD	0,0372474	1	0,0372474	55,31	**0,0000**
CD	0,000279159	1	0,000279159	0,41	0,5329
Total Error	0,00740776	11	0,000673432		
Total (corrected)	0,230575	21			
R^2	96,7873 %				
Adj - R^2	93,8666 %				
Standard error	0,0259506				
Std. Dev	0,0136648				

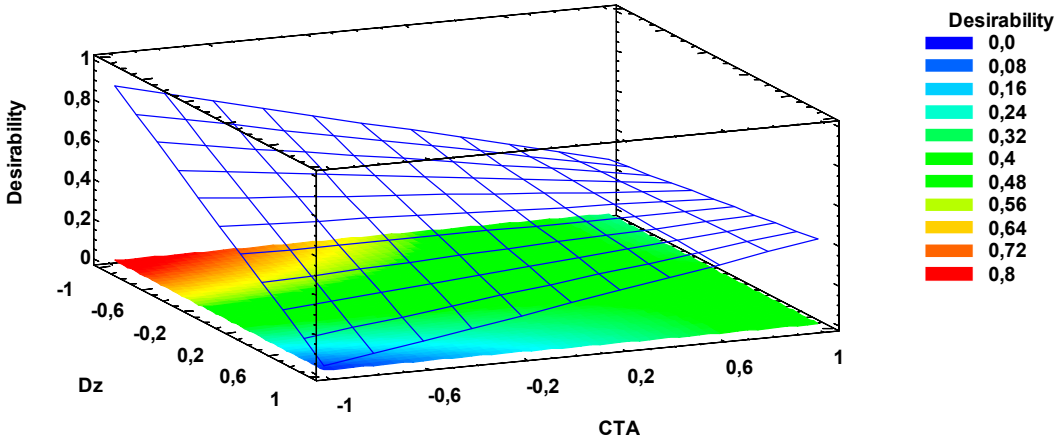


Figure S4. Response surface and contour plots of the multivariate analysis performed with the M1 process method for the system Dz – Cd(II), when 2NPOE = Time = 0,0.

For the Dz – Cd(II) system, the equations model was:

D = 0.400003 - 0.177793*Dz - 0.0481715*CTA + 0.12176*Time*Dz + 0.251488*Dz*CTA (S2)

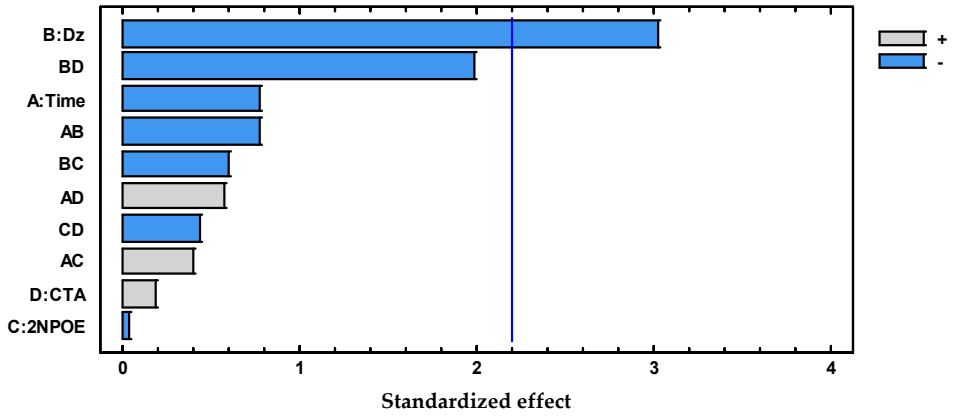


Figure S5. Pareto of the multivariate analysis performed with the M1 process method for the system Dz – Pb(II).

Table S4. ANOVA values of the multivariate analysis performed with the M1 process method for the system Dz – Pb(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,0106482	1	0,0106482	0,60	0,4558
B:Dz	0,162817	1	0,162817	9,14	**0,0116**
C:2NPOE	0,0000254771	1	0,0000254771	0,00	0,9705
D:CTA	0,000659052	1	0,000659052	0,04	0,8510
AB	0,0106383	1	0,0106383	0,60	0,4560
AC	0,00286615	1	0,00286615	0,16	0,6960
AD	0,0058389	1	0,0058389	0,33	0,5785
BC	0,00634343	1	0,00634343	0,36	0,5628
BD	0,0699709	1	0,0699709	3,93	0,0731
CD	0,00349611	1	0,00349611	0,20	0,6664
Total Error	0,195983	11	0,0178166		
Total (corrected)	0,480365	21			
R^2	59,2012 %				
Adj - R^2	22,1114 %				
Standard error	0,133479				
Std. Dev	0,0646804				

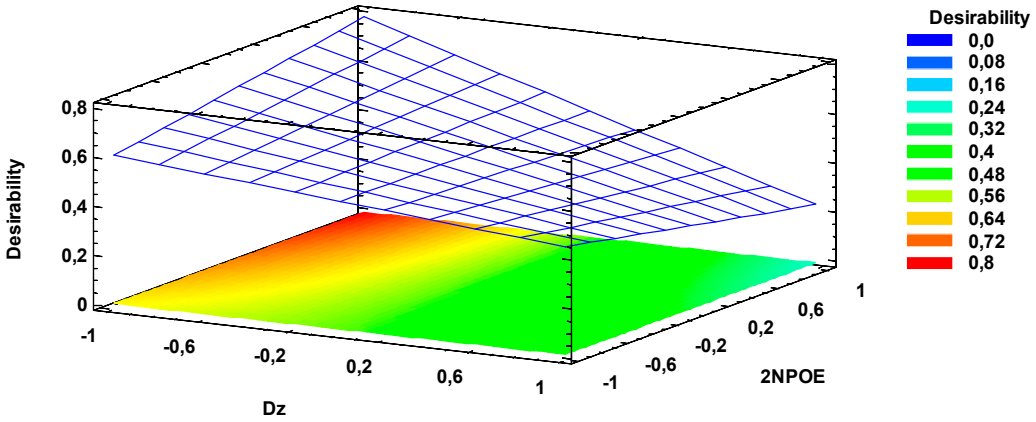


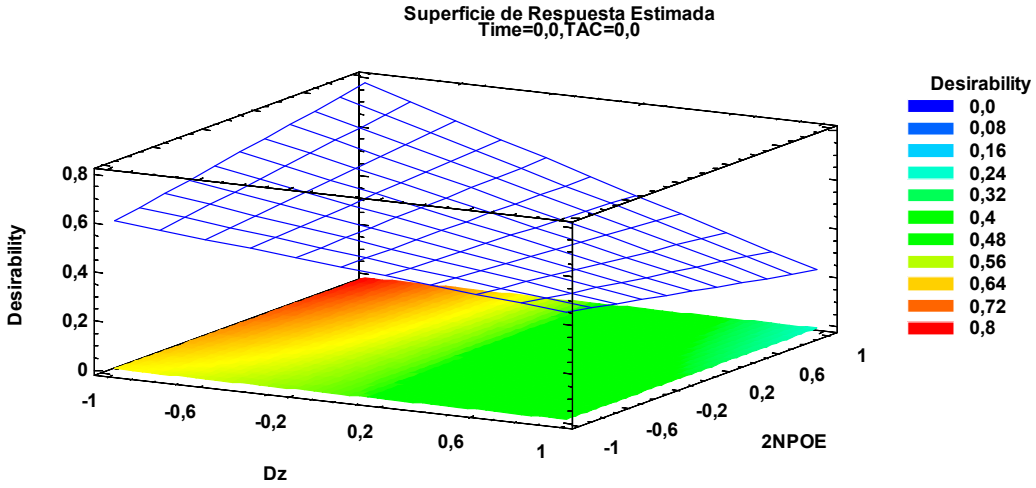
Figure S6. Response surface and contour plots of the multivariate analysis performed with the M1 process method for the system Dz – Pb(II), when CTA = Time = 0,0.

For the system Dz – Pb(II) the model was:

D = 0.517454 - 0.046148*Time - 0.180459*Dz (S3)

Table S5. Values of the predicted desirability of the multivariate analysis performed with the M1 process method using PAN as chromophore.

Experimental runs	Response		
	Expected Desirability		
	PAN – Cd(II)	PAN – Pb(II)	PAN – Hg(II)
1	0.412899	0.706786	0.554163
2	0.412899	0.706786	0.554163
3	0.239581	0.791831	0.531357
4	0.351363	0.770515	0.554544
5	0.384996	0.628514	0.568758
6	0.412899	0.706786	0.554163
7	0.614606	0.489938	0.503729
8	0.451523	0.663153	0.545871
9	0.550099	0.491027	0.367459
10	0.462867	0.343253	0.503729
11	0.469964	0.61407	0.545871
12	0.526763	0.454684	0.367459
13	0.180432	0.554761	0.531357
14	0.294723	0.739257	0.547071
15	0.242642	0.620121	0.475916
16	0.365713	0.713486	0.554544
17	0.504092	0.544041	0.52937
18	0.440114	0.554518	0.442246
19	0.364699	0.581995	0.568758
20	0.320985	0.3661	0.800616
21	0.383758	0.554518	0.647003
22	0.412899	0.706786	0.554163



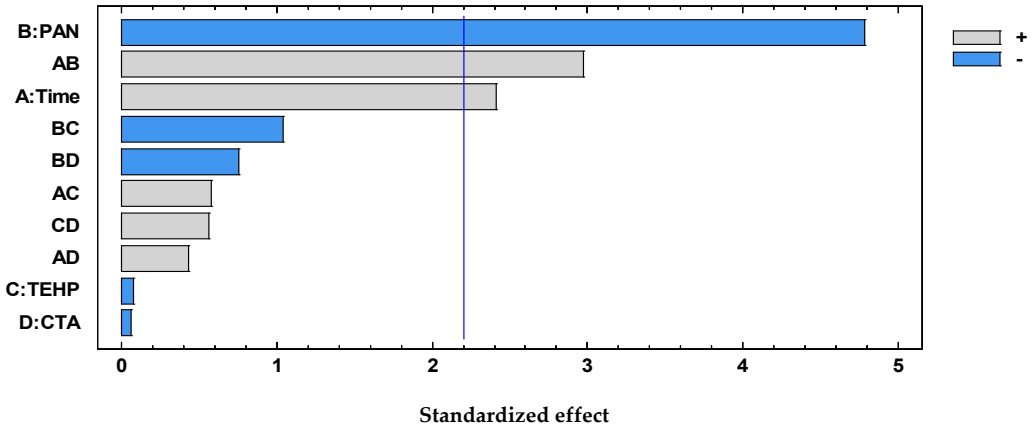


Figure S7. Pareto of the multivariate analysis performed with the M2 process method for the system PAN – Cd(II).

Table S5. ANOVA values of the multivariate analysis performed with the M1 process method for the system PAN – Cd(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,0274138	1	0,0274138	5,82	**0,0344**
B:PAN	0,107617	1	0,107617	22,86	**0,0006**
C:THEP	0,0000307475	1	0,0000307475	0,01	0,9370
D:CTA	0,0000184635	1	0,0000184635	0,00	0,9512
AB	0,0415196	1	0,0415196	8,82	**0,0127**
AC	0,0015598	1	0,0015598	0,33	0,5764
AD	0,000867428	1	0,000867428	0,18	0,6760
BC	0,00509963	1	0,00509963	1,08	0,3203
BD	0,00270399	1	0,00270399	0,57	0,4644
CD	0,00150323	1	0,00150323	0,32	0,5833
Total Error	0,0517731	11	0,00470665		
Total (corrected)	0,264118	21			
R^2	80,3977 %				
Adj - R^2	62,5774 %				
Standard error	0,068605				
Std. Dev	0,0320632				

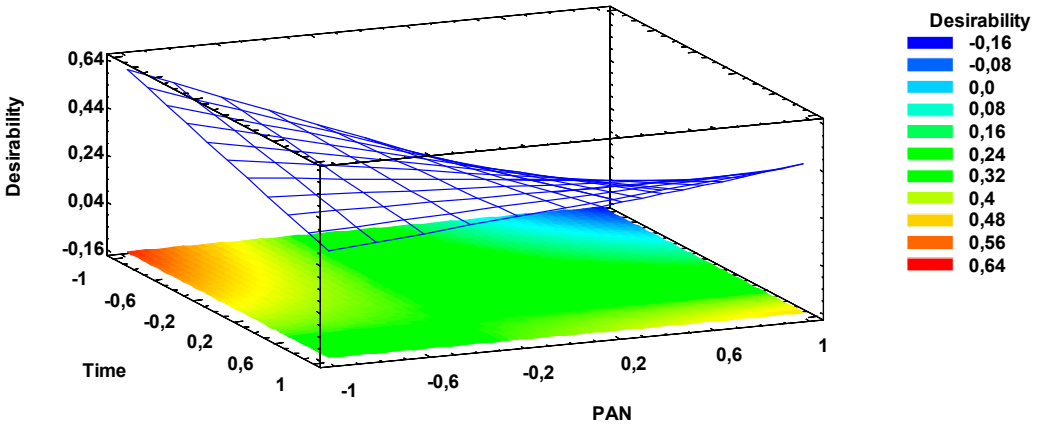


Figure S8. Response surface and contour plots of the multivariate analysis performed with the M1 process method for the system PAN – Cd(II), when CTA = Time = 0,0.

For the system PAN – Cd(II) the model was:

D = 0.3001 + 0.0740457*Time - 0.146713*PAN + 0.235293*Time*PAN (S4)

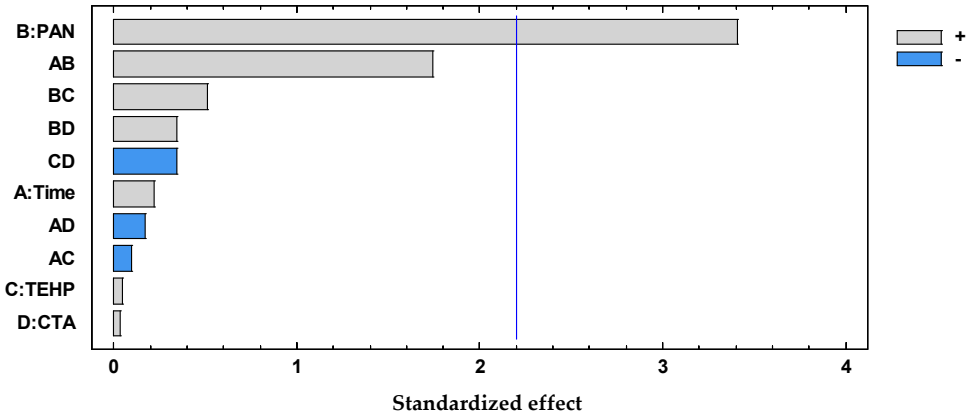


Figure S9. Pareto of the multivariate analysis performed with the M2 process method for the system PAN – Pb(II).

Table S6. ANOVA values of the multivariate analysis performed with the M1 process method for the system PAN – Pb(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,000588688	1	0,000588688	0,05	0,8297
B:PAN	0,14116	1	0,14116	11,63	**0,0058**
C:THEP	0,0000255253	1	0,0000255253	0,00	0,9642
D:CTA	0,0000136384	1	0,0000136384	0,00	0,9739

AB	0,036817	1	0,036817	3,03	0,1095
AC	0,00010842	1	0,00010842	0,01	0,9264
AD	0,000350622	1	0,000350622	0,03	0,8681
BC	0,00317229	1	0,00317229	0,26	0,6193
BD	0,00142016	1	0,00142016	0,12	0,7388
CD	0,00141152	1	0,00141152	0,12	0,7395
Total Error	0,133535	11	0,0121396		
Total (corrected)	0,324055	21			
R^2	58,7924 %				
Adj - R^2	21,3309 %				
Standard error	0,11018				
Std. Dev	0,0749911				

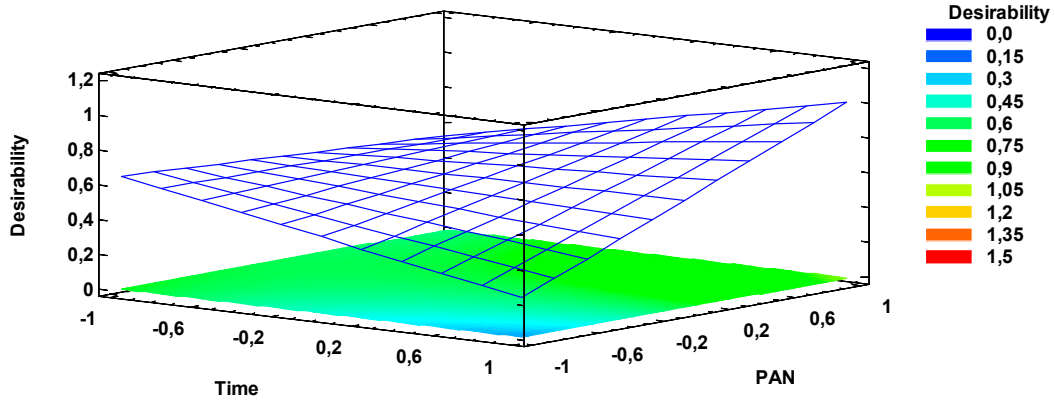


Figure S10. Response surface and contour plots of the multivariate analysis performed with the M1 process method for the system PAN – Pb(II), when CTA = Time = 0,0.

For the system PAN – Pb(II) the model was:

$$D = 0.604665 + 0.168028*PAN \quad (S5)$$

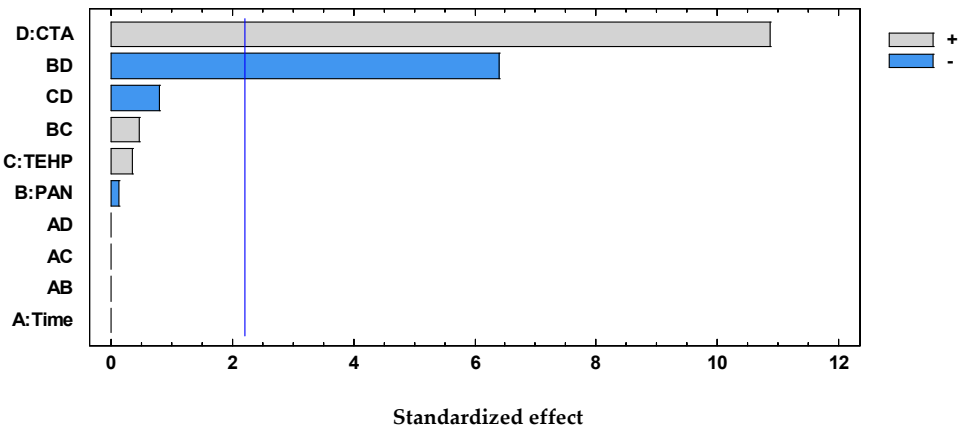


Figure S11. Pareto of the multivariate analysis performed with the M1 process method for the system PAN – Hg(II).

Table S7. ANOVA values of the multivariate analysis performed with the M1 process method for the system PAN – Hg(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,0	1	0,0	0,00	1,0000
B:PAN	0,000013335	1	0,000013335	0,01	0,9062
C:THEP	0,000103831	1	0,000103831	0,11	0,7429
D:CTA	0,108594	1	0,108594	118,34	**0,0000**
AB	0,0	1	0,0	0,00	1,0000
AC	0,0	1	0,0	0,00	1,0000
AD	0,0	1	0,0	0,00	1,0000
BC	0,000192123	1	0,000192123	0,21	0,6562
BD	0,0376356	1	0,0376356	41,01	**0,0001**
CD	0,000583345	1	0,000583345	0,64	0,4421
Total Error	0,010094	11	0,00091764		
Total (corrected)	0,158191	21			
R^2	93,6191 %				
Adj – R^2	87,8183 %				
Standard error	0,0302926				
Std. Dev	0,0176483				

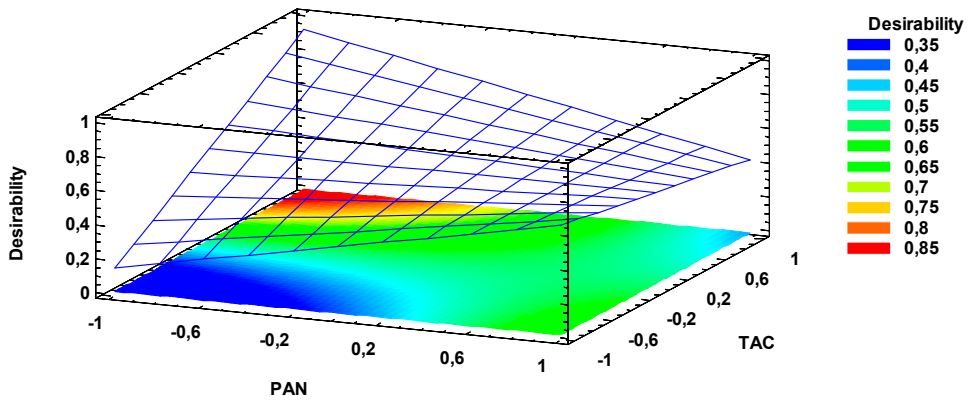
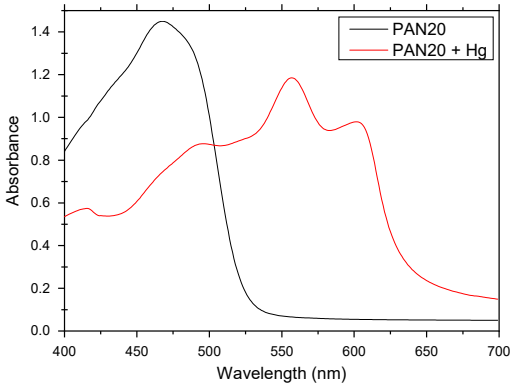
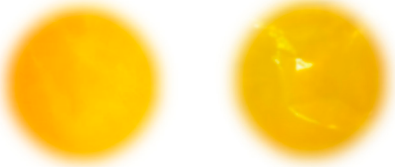
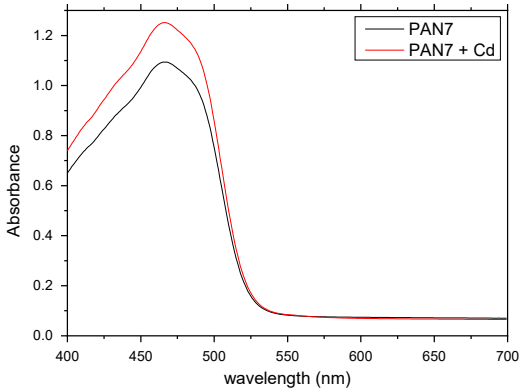
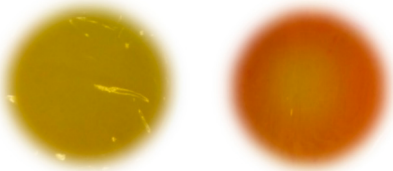
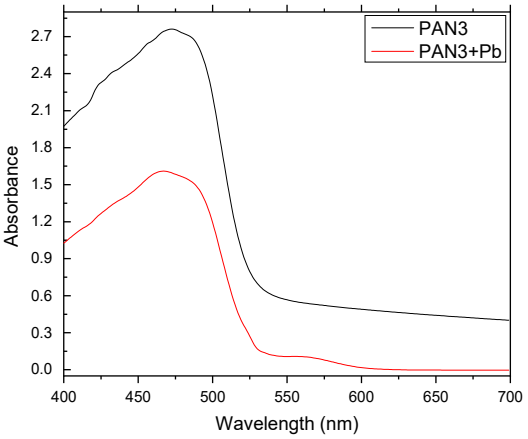


Figure S12. Response surface and contour plots of the multivariate analysis performed with the M1 process method for the system PAN – Hg(II), when CTA = Time = 0,0.

For the system PAN – Hg(II) the model was:

Desirability = 0.536483 + 0.147293*CTA - 0.252795*PAN*CTA (S6)

Table S8. Optimization results using the score values of the first two principal components of PCA for membranes after complexation.

	Optimal experiment	Appearance of the membrane		Spectral
		Before	After	
PAN + Hg	20			
PAN + Cd	7			
PAN + Pb	3			

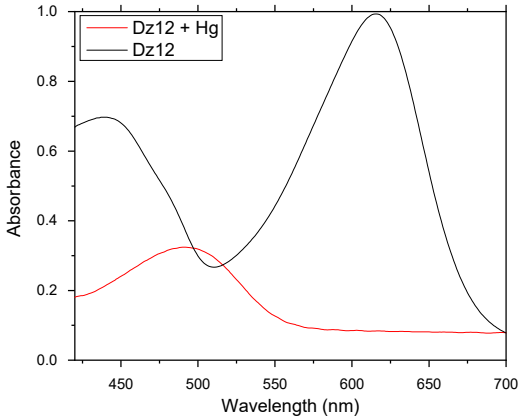
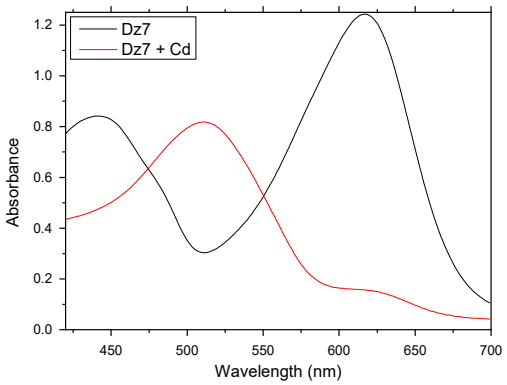
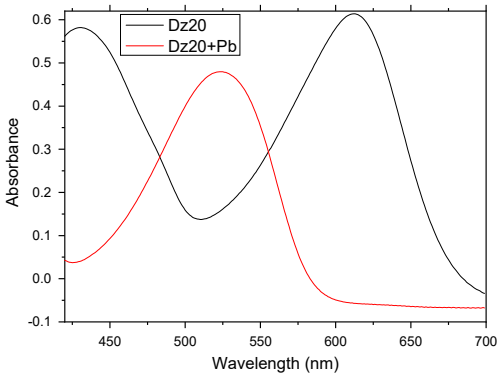
Dz + Hg	12		
Dz + Cd	7		
Dz + Pb	20		

Table S9. Values of the predicted desirability of the multivariate analysis performed with the M2 process method using Dz as chromophore.

Experimental runs	Response		
	Expected Desirability		
	Dz – Cd(II)	Dz – Pb(II)	Dz – Hg(II)
1	0.51468	0.393941	0.424206
2	0.51468	0.393941	0.424206
3	0.463657	0.421779	0.469021
4	0.523088	0.504251	0.396784
5	0.523088	0.471888	0.638758
6	0.51468	0.393941	0.424206
7	0.61753	0.618092	0.469021
8	0.553152	0.491403	0.45976
9	0.553152	0.509909	0.658187
10	0.294094	0.058451	0.469021
11	0.480357	0.385322	0.45976
12	0.480357	0.352591	0.172919
13	0.358429	0.51855	0.469021
14	0.465424	0.403001	0.474017
15	0.465424	0.415281	0.494842
16	0.470733	0.46169	0.396784
17	0.507994	0.160018	0.41322
18	0.51468	0.424416	0.447355
19	0.470733	0.417626	0.167815
20	0.507994	0.284859	0.48104
21	0.51468	0.360902	0.490509
22	0.51468	0.393941	0.424206

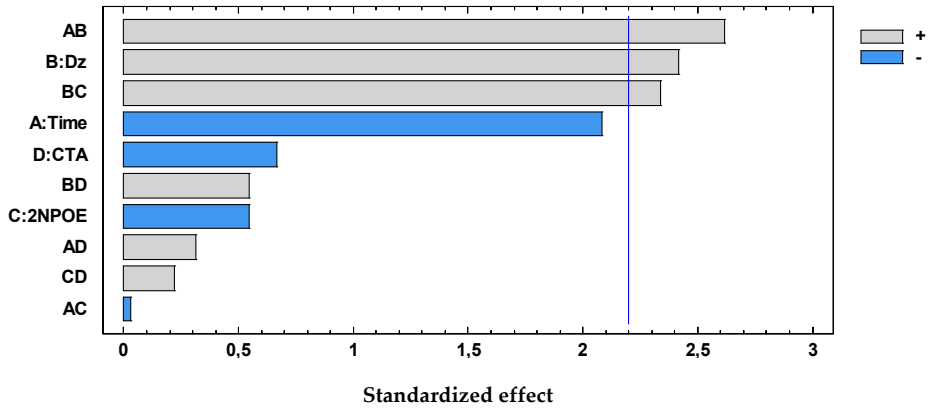


Figure S13. Pareto of the multivariate analysis performed with the M2 process method for the system Dz – Pb(II).

Table S10. ANOVA values of the multivariate analysis performed with the M2 process method for the system Dz – Pb(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,0338655	1	0,0338655	4,33	0,0616
B:Dz	0,0456172	1	0,0456172	5,83	**0,0343**
C:2NPOE	0,00233103	1	0,00233103	0,30	0,5960
D:CTA	0,00349265	1	0,00349265	0,45	0,5178
AB	0,0535622	1	0,0535622	6,85	**0,0240**
AC	0,00000763568	1	0,00000763568	0,00	0,9756
AD	0,000762204	1	0,000762204	0,10	0,7608
BC	0,0427957	1	0,0427957	5,47	**0,0392**
BD	0,0023428	1	0,0023428	0,30	0,5951
CD	0,000383735	1	0,000383735	0,05	0,8288
Total Error	0,0860455	11	0,00782232		
Total (corrected)	0,295103	21			
R^2	70,8422 %				
Adj - R^2	44,3351 %				
Standard error	0,0884439				
Std. Dev	0,0459284				

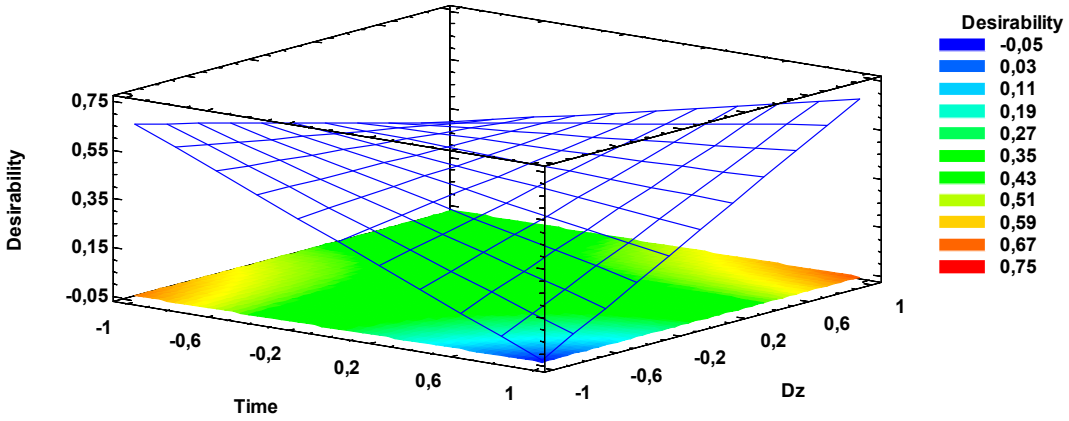


Figure S14. Response surface and contour plots of the multivariate analysis performed with the M2 process method for the system Dz – Pb(II), when CTA = 2NPOE = 0,0.

For the system Dz – Pb(II) the model was:

$$D = 0{,}401601 + 0{,}0955195*Dz + 0{,}267246*Time*Dz - 0{,}00356558*Time*2NPOE \quad (S7)$$

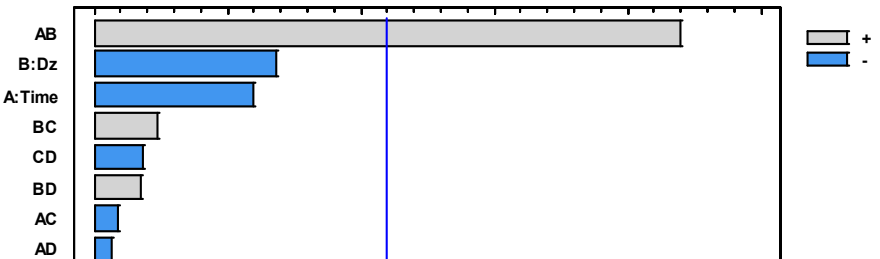


Figure S8. Pareto of the multivariate analysis performed with the M2 process method for the system Dz – Cd(II).

Table S11. ANOVA values of the multivariate analysis performed with the M2 process method for the system Dz – Cd(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,00335633	1	0,00335633	1,41	0,2599
B:Dz	0,00447673	1	0,00447673	1,88	0,1974
C:2NPOE	0,00000180301	1	0,00000180301	0,00	0,9785
D:CTA	0,00000108269	1	0,00000108269	0,00	0,9834
AB	0,0459382	1	0,0459382	19,32	**0,0011**
AC	0,0000720997	1	0,0000720997	0,03	0,8649
AD	0,0000400958	1	0,0000400958	0,02	0,8990
BC	0,000540699	1	0,000540699	0,23	0,6428
BD	0,000286766	1	0,000286766	0,12	0,7350
CD	0,000318967	1	0,000318967	0,13	0,7212
Total Error	0,0261616	11	0,00237833		
Total (corrected)	0,0891673	21			
R^2	70,66 %				
Adj - R^2	43,9874 %				
Standard error	0,0487681				
Std. Dev	0,0217078				

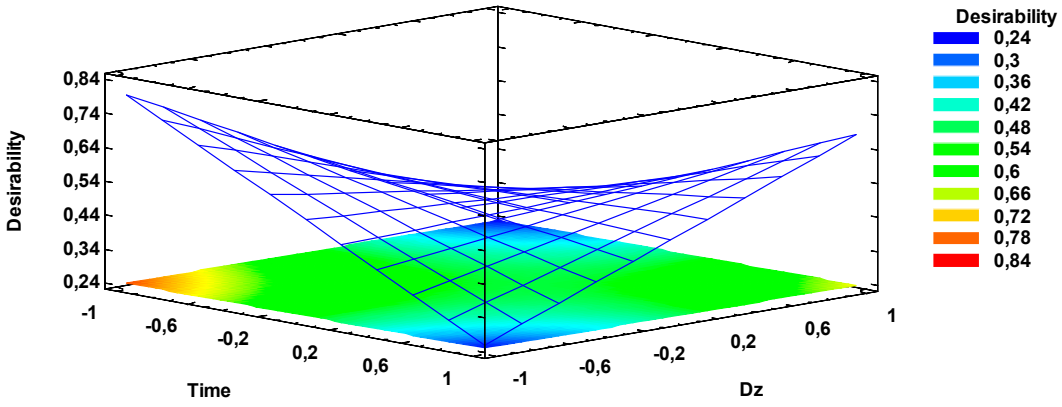


Figure S14. Response surface and contour plots of the multivariate analysis performed with the M2 process method for the system Dz – Cd(II), when CTA = 2NPOE = 0,0.

For the system Dz – Cd(II) the model was:

$$D = 0{,}491962 + 0{,}247497*Time*Dz \quad \text{(S8)}$$

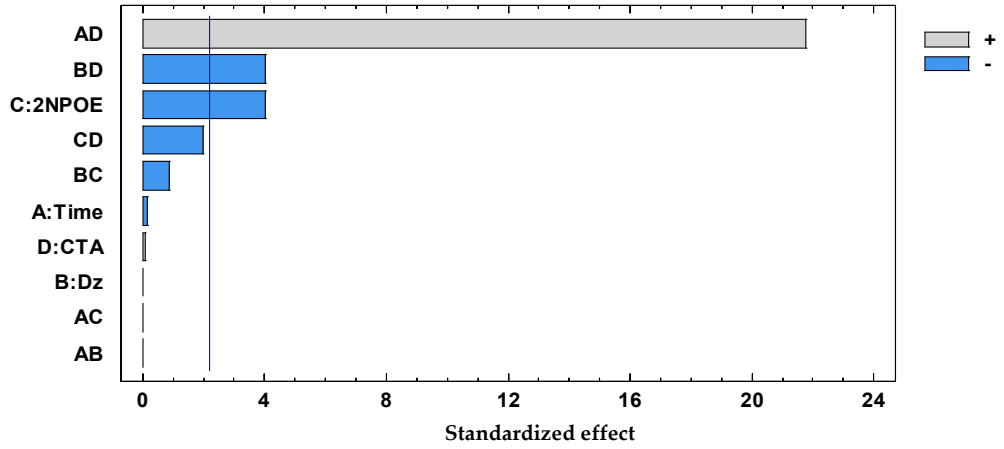


Figure S15. Pareto of the multivariate analysis performed with the M2 process method for the system Dz – Hg(II).

Table S12. ANOVA values of the multivariate analysis performed with the M2 process method for the system Dz – Hg(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,0000102603	1	0,0000102603	0,02	0,8799
B:Dz	2,76061E-8	1	2,76061E-8	0,00	0,9937
C:2NPOE	0,00697371	1	0,00697371	16,26	**0,0020**
D:CTA	0,00000281379	1	0,00000281379	0,01	0,9369
AB	0,0	1	0,0	0,00	1,0000
AC	0,0	1	0,0	0,00	1,0000
AD	0,203179	1	0,203179	473,82	**0,0000**
BC	0,000314633	1	0,000314633	0,73	0,4099
BD	0,00700015	1	0,00700015	16,32	**0,0019**
CD	0,00166447	1	0,00166447	3,88	0,0745
Total Error	0,00471694	11	0,000428812		
Total (corrected)	0,250491	21			
R^2	98,1169 %				
Adj - R^2	96,405 %				
Standard error	0,0207078				
Std. Dev	0,0113725				

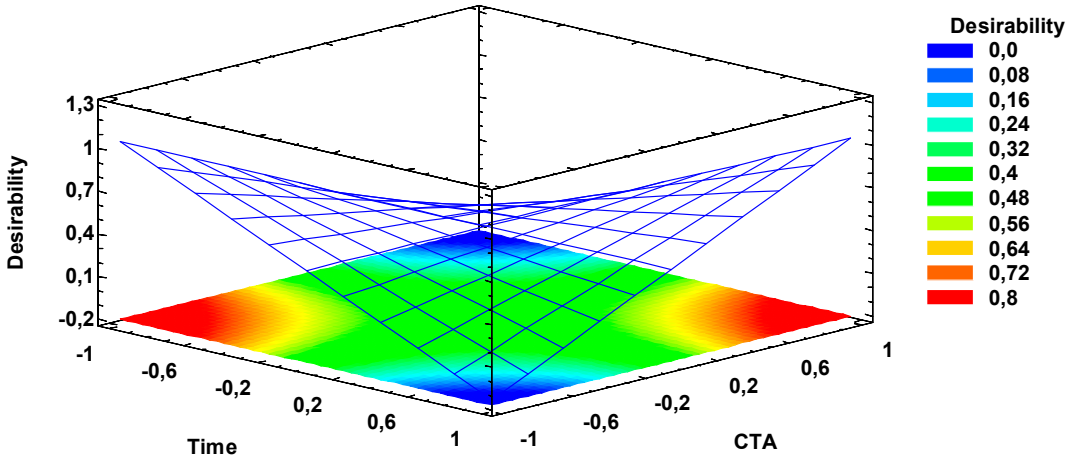


Figure S16. Response surface and contour plots of the multivariate analysis performed with the M2 process method for the system Dz – Hg(II), when Dz = 2NPOE = 0,0.

For the system Dz – Hg(II) the model was:

D = 0.442036 - 0.0373232*2NPOE + 0.604432*Time*CTA - 0.109024*Dz*CTA (S9)

Table S13. Values of the predicted desirability of the multivariate analysis performed with the M2 process method using PAN as chromophore.

Experimental runs	Response		
	Expected Desirability		
	PAN – Hg(II)	PAN – Pb(II)	PAN – Cd(II)
1	0.543436	0.548901	0.271829
2	0.543436	0.548901	0.271829
3	0.41037	0.613708	0.278323
4	0.521259	0.578848	0.317035
5	0.521259	0.578848	0.317035
6	0.543436	0.548901	0.271829
7	0.503639	0.309131	0.260751
8	0.547868	0.473295	0.312326
9	0.547868	0.473295	0.312326
10	0.503639	0.358989	0.0
11	0.547868	0.505125	0.147643
12	0.547868	0.505125	0.147643
13	0.41037	0.71269	0.135137
14	0.479064	0.64868	0.390385
15	0.479064	0.64868	0.260751
16	0.521259	0.617777	0.229745
17	0.535071	0.426379	0.184666
18	0.543436	0.548901	0.271829
19	0.521259	0.617777	0.229745
20	0.535071	0.426379	0.184666
21	0.543436	0.548901	0.271829
22	0.543436	0.548901	0.271829

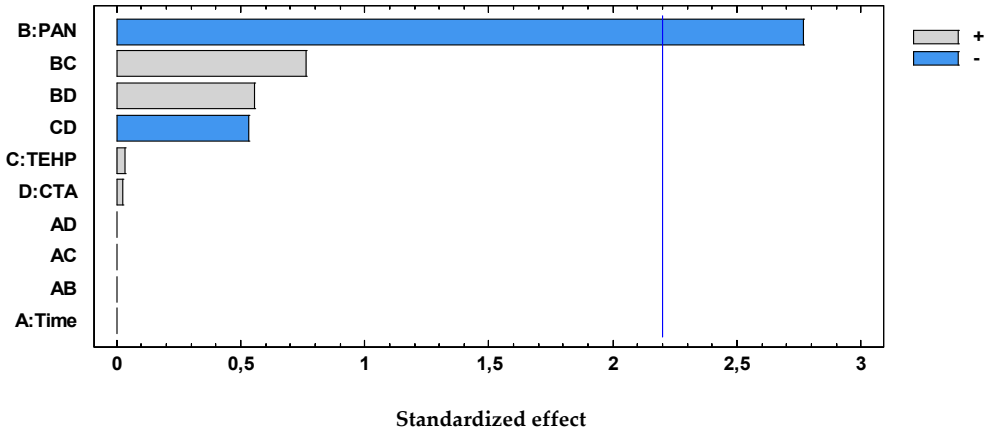


Figure S17. Pareto of the multivariate analysis performed with the M2 process method for the system PAN – Hg(II).

Table S14. ANOVA values of the multivariate analysis performed with the M2 process method for the system PAN – Hg(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,0	1	0,0	0,00	1,0000
B:PAN	0,013204	1	0,013204	7,65	**0,0183**
C:THEP	0,00000174217	1	0,00000174217	0,00	0,9752
D:CTA	0,00000104615	1	0,00000104615	0,00	0,9808
AB	0,0	1	0,0	0,00	1,0000
AC	0,0	1	0,0	0,00	1,0000
AD	0,0	1	0,0	0,00	1,0000
BC	0,00100899	1	0,00100899	0,58	0,4605
BD	0,000535092	1	0,000535092	0,31	0,5887
CD	0,000489681	1	0,000489681	0,28	0,6048
Total Error	0,018974	11	0,00172491		
Total (corrected)	0,0346883	21			
R^2	45,3013%				
Adj - R^2	0,0%				
Standard error	0,0415321				
Std. Dev	0,0221346				

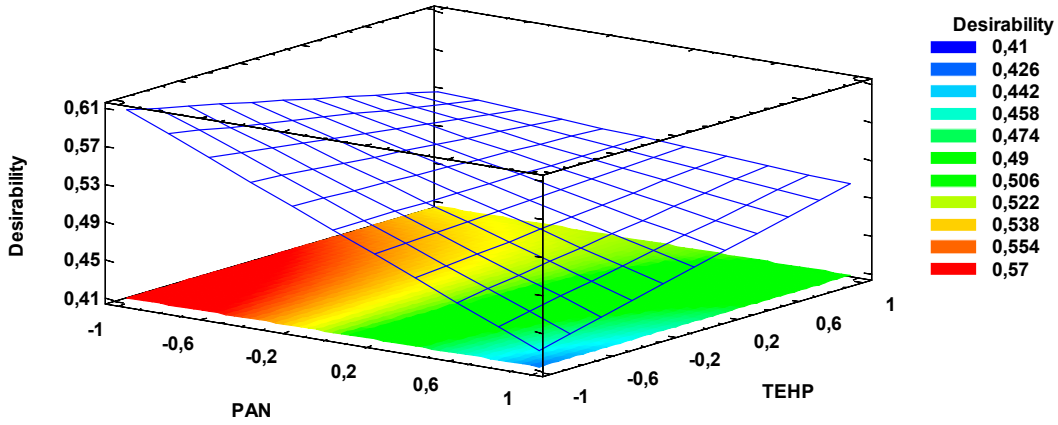


Figure S18. Response surface and contour plots of the multivariate analysis performed with the M2 process method for the system PAN – Hg(II), when CTA = Time = 0,0.

For the system PAN – Hg(II) the model was:

$$D = 0.517875 + 0.0*Time - 0.0513902*PAN \quad (S10)$$

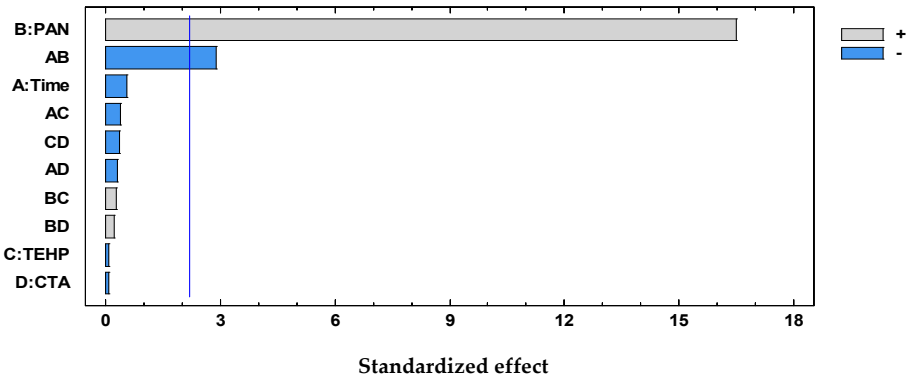


Figure S19. Pareto of the multivariate analysis performed with the M2 process method for the system PAN – Pb(II).

Table S13. ANOVA values of the multivariate analysis performed with the M2 process method for the system PAN – Pb(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,000200484	1	0,000200484	0,30	0,5941
B:PAN	0,181549	1	0,181549	272,70	**0,0000**
C:THEP	0,00000417595	1	0,00000417595	0,01	0,9383
D:CTA	0,00000250761	1	0,00000250761	0,00	0,9522
AB	0,00553834	1	0,00553834	8,32	**0,0149**
AC	0,000100039	1	0,000100039	0,15	0,7057
AD	0,0000556332	1	0,0000556332	0,08	0,7779
BC	0,0000519484	1	0,0000519484	0,08	0,7852
BD	0,0000275653	1	0,0000275653	0,04	0,8425
CD	0,0000784508	1	0,0000784508	0,12	0,7379
Total Error	0,00732311	11	0,000665738		
Total (corrected)	0,197303	21			
R^2	96,2884 %				
Adj - R^2	92,9142 %				
Standard error	0,0258019				
Std. Dev	0,0135246				

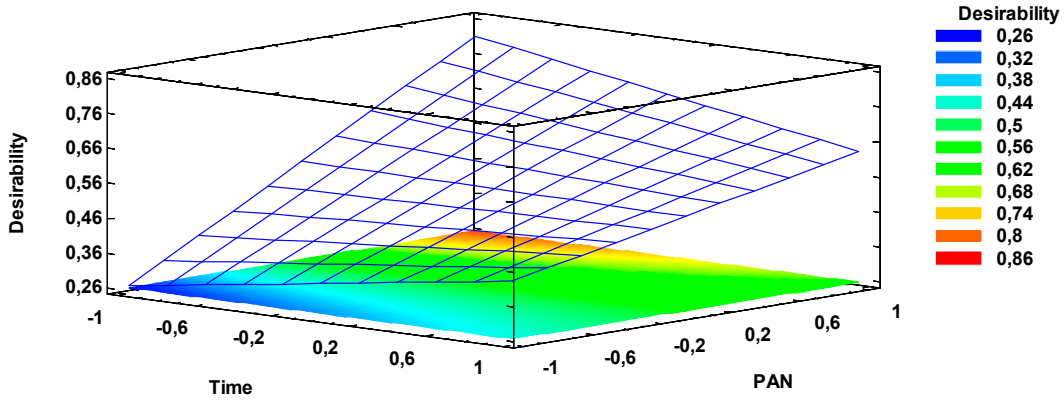


Figure S20. Response surface and contour plots of the multivariate analysis performed with the M2 process method for the system PAN – Pb(II), when CTA = THEP = 0,0.

For the system PAN – Pb(II) the model was:

D = 0.535822 + 0.190557*PAN - 0.0859353*Time*PAN (S11)

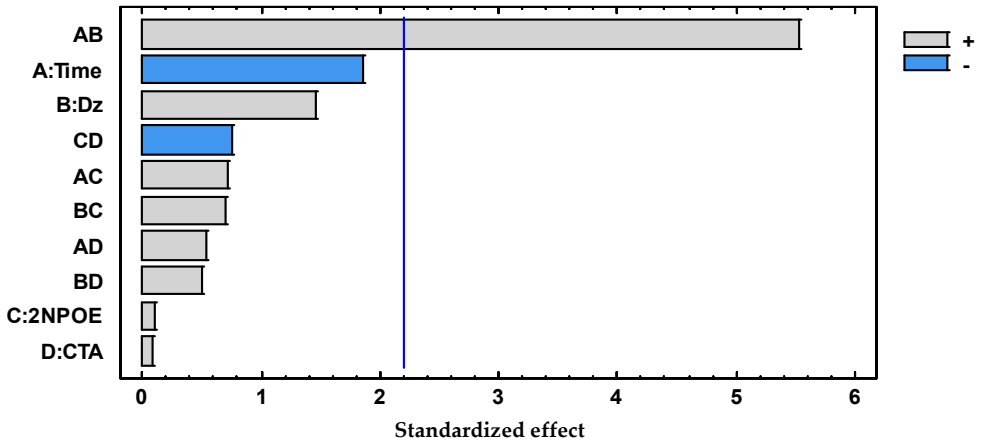


Figure S21. Pareto of the multivariate analysis performed with the M2 process method for the system PAN – Cd(II).

Table S14. ANOVA values of the multivariate analysis performed with the M2 process method for the system PAN – Cd(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,0080796	1	0,0080796	3,47	0,0892
B:PAN	0,00499023	1	0,00499023	2,15	0,1710
C:THEP	0,0000236866	1	0,0000236866	0,01	0,9214
D:CTA	0,0000142235	1	0,0000142235	0,01	0,9391
AB	0,0711745	1	0,0711745	30,60	**0,0002**
AC	0,00122884	1	0,00122884	0,53	0,4825
AD	0,000683379	1	0,000683379	0,29	0,5986
BC	0,0011196	1	0,0011196	0,48	0,5022
BD	0,000594004	1	0,000594004	0,26	0,6233
CD	0,00133417	1	0,00133417	0,57	0,4647
Total Error	0,0255845	11	0,00232587		
Total (corrected)	0,145186	21			
R^2	82,3781 %				
Adj - R^2	66,3581 %				
Standard error	0,0482272				

Std. Dev	0,0243175

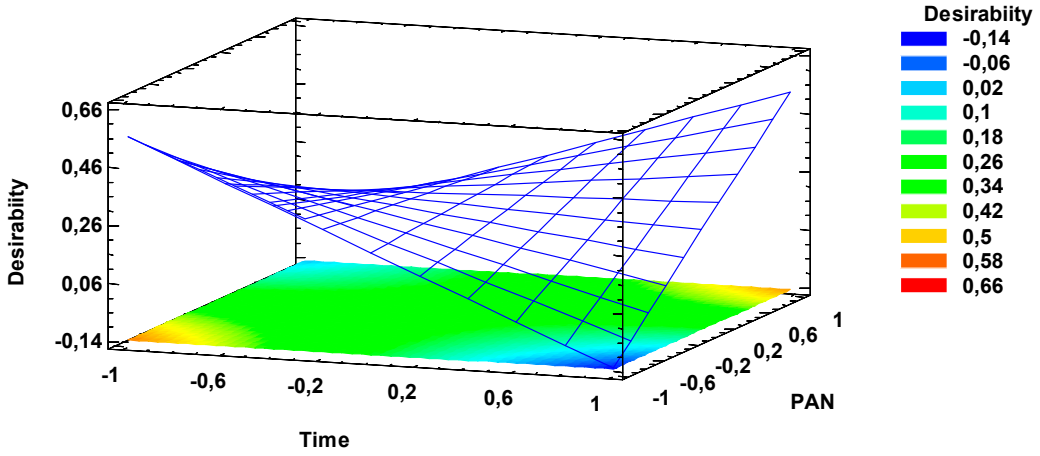


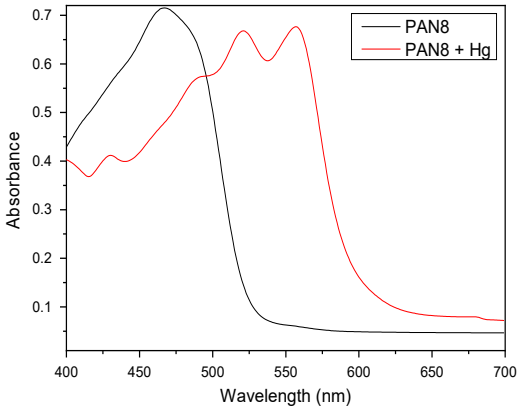
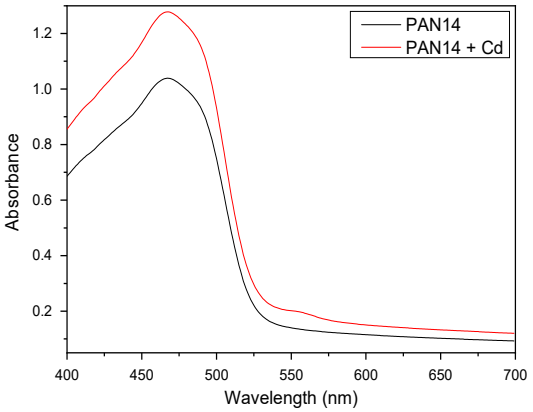
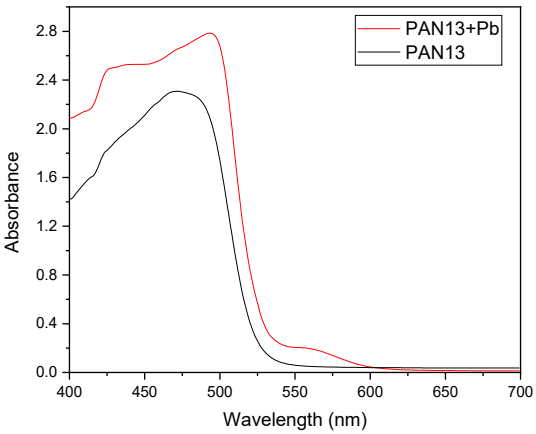
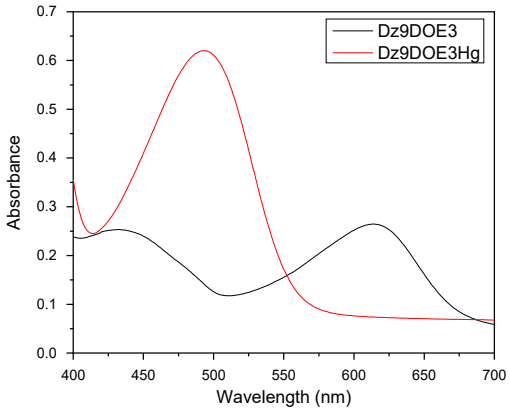
Figure S22. Response surface and contour plots of the multivariate analysis performed with the M2 process method for the system PAN – Cd(II), when CTA = THEP = 0,0.

For the system PAN – Cd(II) the model was:

$$D = 0.242679 + 0.308066*Time*PAN \quad (S12)$$

Table S15. Optimization results using the absorbance values before and after complexation.

Optimal experiment	Appearance of the membrane		Spectral
	Before	After	

PAN + Hg	8			
PAN + Cd	14			
PAN + Pb	13			
Dz + Hg	9			

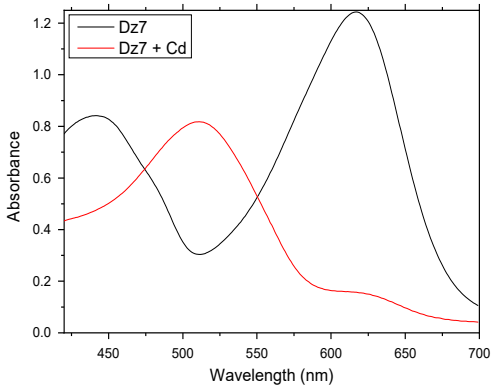
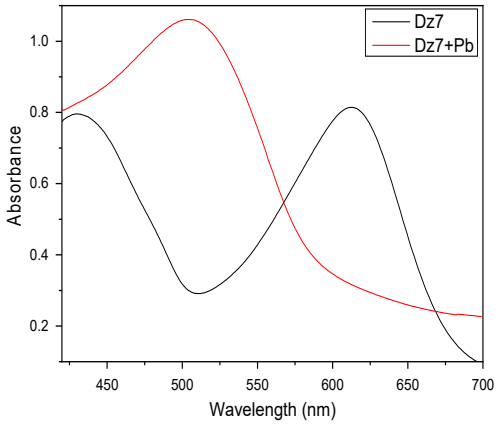
Dz + Cd	7			
Dz + Pb	7			

Table S17. Values of the predicted desirability of the multivariate analysis performed with the M3 process method using Dz as chromophore.

Experimental runs	Response		
	Expected Desirability		
	Dz – Cd(II)	Dz – Pb(II)	Dz – Hg(II)
1	0.179692	0.561281	0.685941
2	0.179692	0.561281	0.685941
3	0.269257	0.674154	0.667604
4	0.0	0.601309	0.597549
5	0.0	0.89867	0.896816
6	0.179692	0.561281	0.685941
7	0.494816	0.419034	0.667604
8	0.365697	0.51817	0.597549
9	0.260604	0.46735	0.896816
10	0.324142	0.419034	0.218987
11	0.319801	0.51817	0.708166
12	0.237532	0.194255	0.668952
13	0.176383	0.674154	0.218987
14	0.288784	0.638707	0.592996
15	0.0821848	0.477594	0.700103
16	0.0	0.601309	0.708166
17	0.230607	0.471302	0.592996
18	0.28994	0.401814	0.809836
19	0.0	0.592225	0.668952
20	0.173462	0.63269	0.700103
21	0.331309	0.720747	0.809836
22	0.179692	0.561281	0.685941

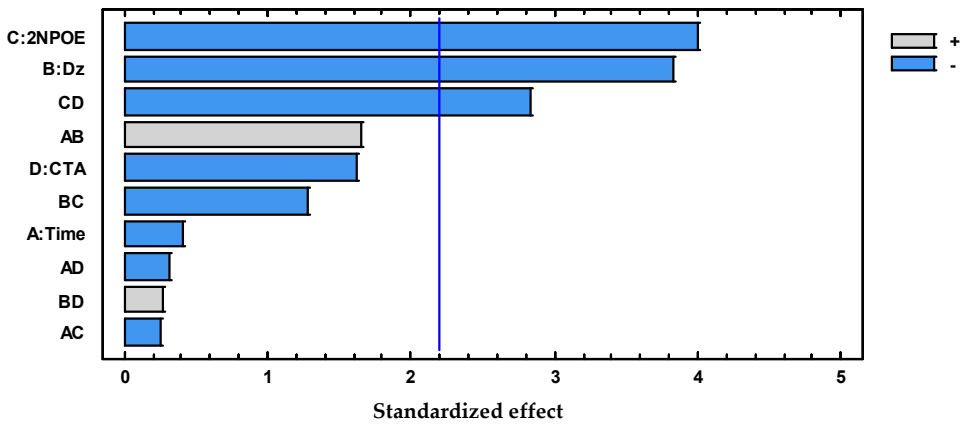


Figure S23. Pareto of the multivariate analysis performed with the M3 process method for the system Dz – Cd(II).

Table S18. ANOVA values of the multivariate analysis performed with the M3 process method for the system Dz – Cd(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,00107704	1	0,00107704	0,17	0,6891
B:Dz	0,0935983	1	0,0935983	14,66	**0,0028**
C:2NPOE	0,102334	1	0,102334	16,03	**0,0021**
D:CTA	0,016699	1	0,016699	2,62	0,1341
AB	0,0173644	1	0,0173644	2,72	0,1273
AC	0,000397844	1	0,000397844	0,06	0,8075
AD	0,000657078	1	0,000657078	0,10	0,7543
BC	0,0104035	1	0,0104035	1,63	0,2280
BD	0,000439125	1	0,000439125	0,07	0,7979
CD	0,0513013	1	0,0513013	8,04	**0,0162**
Total Error	0,0702125	11	0,00638296		
Total (corrected)	0,363744	21			
R^2	80,6973 %				
Adj - R^2	63,1494 %				
Standard error	0,0798934				
Std. Dev	0,0418171				

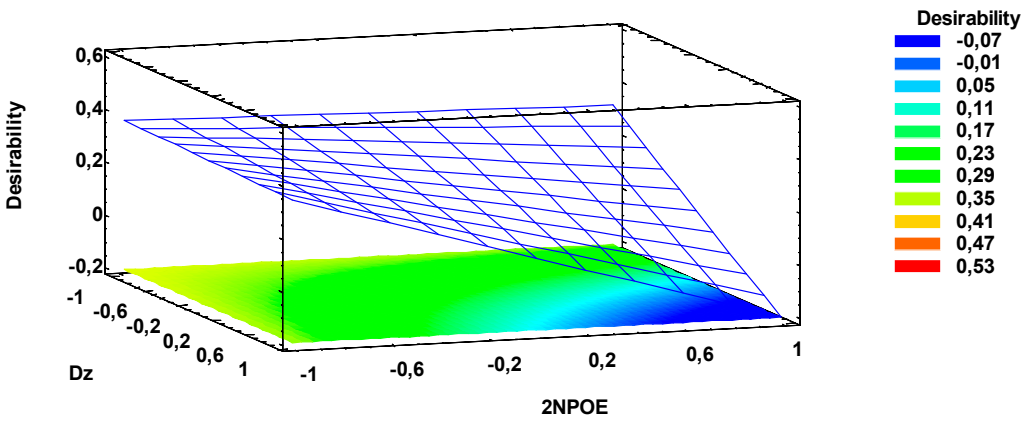


Figure S22. Response surface and contour plots of the multivariate analysis performed with the M3 process method for the system Dz – Cd(II), when CTA = Time = 0,0.

For the system Dz – Cd(II) the model was:

D = 0.207411 - 0.136824*Dz - 0.142974*2NPOE - 0.286167*2NPOE*CTA (13)

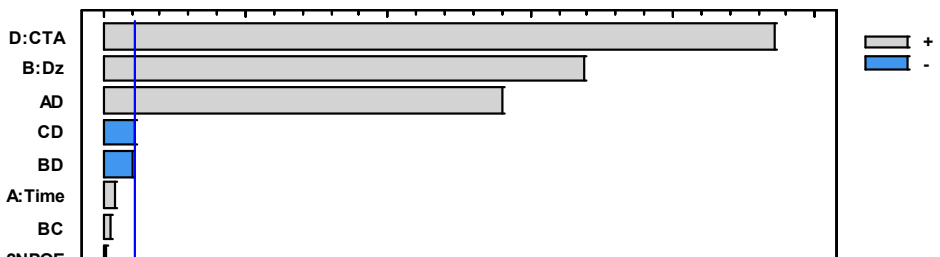


Figure S23. Pareto of the multivariate analysis performed with the M3 process method for the system Dz – Pb(II).

Table S19. ANOVA values of the multivariate analysis performed with the M3 process method for the system Dz – Pb(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,0000556111	1	0,0000556111	0,58	0,4610
B:Dz	0,108452	1	0,108452	1137,88	**0,0000**
C:2NPOE	0,00000389023	1	0,00000389023	0,04	0,8436
D:CTA	0,212235	1	0,212235	2226,78	**0,0000**
AB	0,0	1	0,0	0,00	1,0000
AC	0,0	1	0,0	0,00	1,0000
AD	0,0746342	1	0,0746342	783,07	**0,0000**
BC	0,0000300068	1	0,0000300068	0,31	0,5860
BD	0,000416186	1	0,000416186	4,37	0,0607
CD	0,000457735	1	0,000457735	4,80	0,0508
Total Error	0,00104841	11	0,0000953102		
Total (corrected)	0,406732	21			
R^2	99,7422 %				
Adj - R^2	99,5079 %				
Standard error	0,0097627				
Std. Dev	0,00616977				

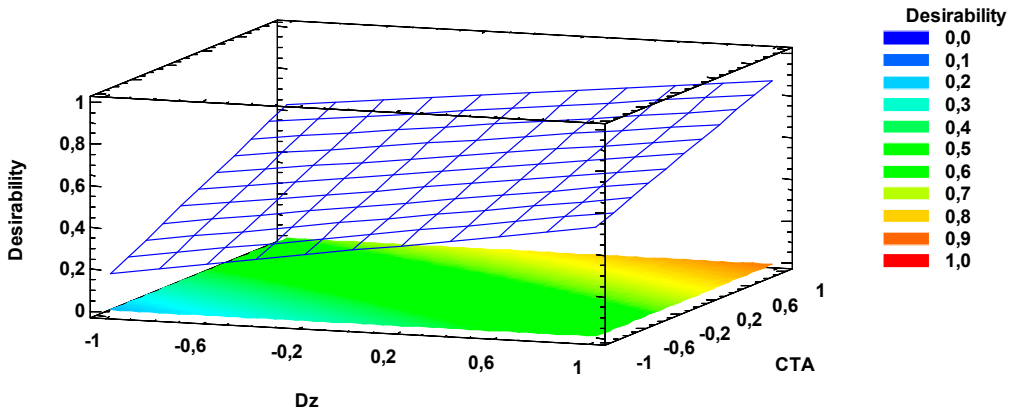


Figure S24. Response surface and contour plots of the multivariate analysis performed with the M3 process method for the system Dz – Pb(II), when 2NPOE = Time = 0,0.

For the system Dz – Pb(II) the model was:

$$D = 0.552991 + 0.147281*Dz + 0.205914*CTA + 0.366334*Time*CTA \quad (S14)$$

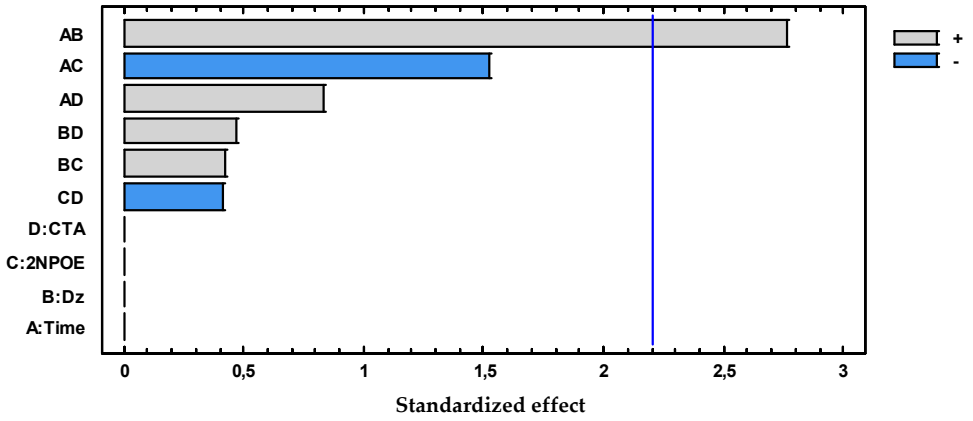


Figure S25. Pareto of the multivariate analysis performed with the M3 process method for the system Dz – Hg(II).

Table S20. ANOVA values of the multivariate analysis performed with the M3 process method for the system Dz – Hg(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,0	1	0,0	0,00	1,0000
B:Dz	0,0	1	0,0	0,00	1,0000
C:2NPOE	0,0	1	0,0	0,00	1,0000
D:CTA	0,0	1	0,0	0,00	1,0000
AB	0,201257	1	0,201257	7,64	**0,0184**
AC	0,0609798	1	0,0609798	2,32	0,1563
AD	0,0182156	1	0,0182156	0,69	0,4233
BC	0,00477106	1	0,00477106	0,18	0,6786
BD	0,00580992	1	0,00580992	0,22	0,6477
CD	0,00449788	1	0,00449788	0,17	0,6873
Total Error	0,289661	11	0,0263329		
Total (corrected)	0,57352	21			
R^2	49,4941 %				
Adj - R^2	3,57966 %				
Standard error	0,162274				
Std. Dev	0,0913344				

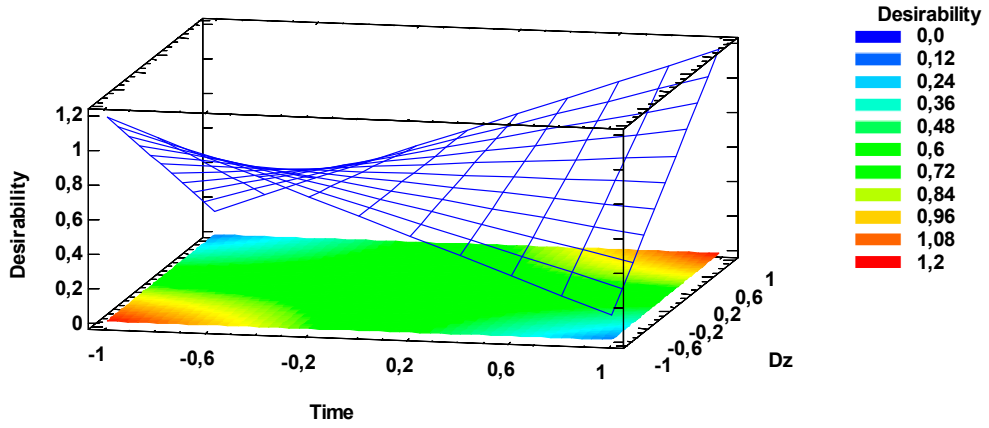


Figure S26. Response surface and contour plots of the multivariate analysis performed with the M3 process method for the system Dz – Hg(II), when 2NPOE = Time = 0,0.

For the system Dz – Hg(II) the model was:

$$D = 0.657514 + 0.518033*Time*Dz \quad (S15)$$

Table S21. Values of the predicted desirability of the multivariate analysis performed with the M3 process method using PAN as chromophore.

Experimental runs	Response		
	Expected Desirability		
	PAN – Cd(II)	PAN – Pb(II)	PAN – Hg(II)
1	0.455591	0.465926	0.416836
2	0.455591	0.223915	0.416836
3	0.430268	0.563115	0.482499
4	0.454742	0.565705	0.401948
5	0.454742	0.392263	0.600185
6	0.455591	0.428557	0.416836
7	0.28149	0.671214	0.433985
8	0.397523	0.643515	0.485418
9	0.397523	0.482728	0.427605
10	0.411835	0.563115	0.433985
11	0.449011	0.565705	0.636049
12	0.449011	0.392263	0.460698
13	0.629506	0.671214	0.482499
14	0.512795	0.261285	0.612344
15	0.512795	0.596423	0.485578
16	0.513641	0.643515	0.574882
17	0.390087	0.261285	0.479722
18	0.455591	0.465926	0.460239
19	0.513641	0.482728	0.646768
20	0.390087	0.596423	0.606119
21	0.455591	0.465926	0.699678
22	0.455591	0.465926	0.416836

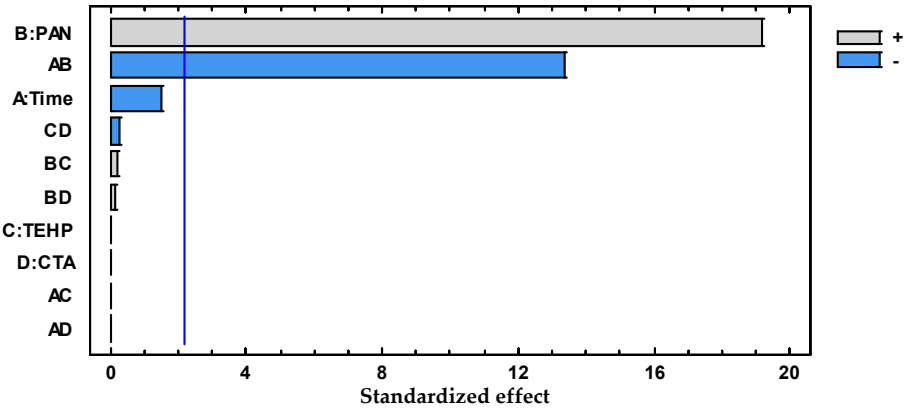


Figure S27. Pareto of the multivariate analysis performed with the M3 process method for the system PAN – Cd(II).

Table S22. ANOVA values of the multivariate analysis performed with the M3 process method for the system PAN – Cd(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,00035041	1	0,00035041	2,30	0,1573
B:PAN	0,0560517	1	0,0560517	368,35	**0,0000**
C:THEP	2,38862E-7	1	2,38862E-7	0,00	0,9691
D:CTA	1,43434E-7	1	1,43434E-7	0,00	0,9761
AB	0,0271562	1	0,0271562	178,46	**0,0000**
AC	3,5837E-8	1	3,5837E-8	0,00	0,9880
AD	1,99296E-8	1	1,99296E-8	0,00	0,9911
BC	0,00000700214	1	0,00000700214	0,05	0,8341
BD	0,00000371548	1	0,00000371548	0,02	0,8787
CD	0,0000103725	1	0,0000103725	0,07	0,7989
Total Error	0,00167386	11	0,000152169		
Total (corrected)	0,0913495	21			
R^2	98,1676 %				
Adj - R^2	96,5018 %				
Standard error	0,0123357				
Std. Dev	0,00509949				

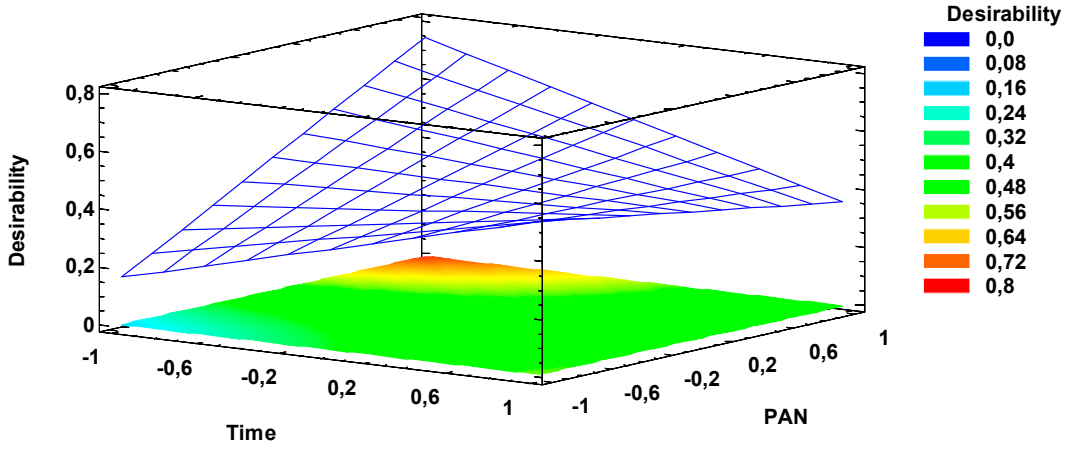


Figure S28. Response surface and contour plots of the multivariate analysis performed with the M3 process method for the system PAN – Cd(II), when THEP = CTA = 0,0.

For the system PAN – Cd(II) the model was:

Desirability= 0.45101 + 0.105882*PAN - 0.19029*Time*PAN (S16)

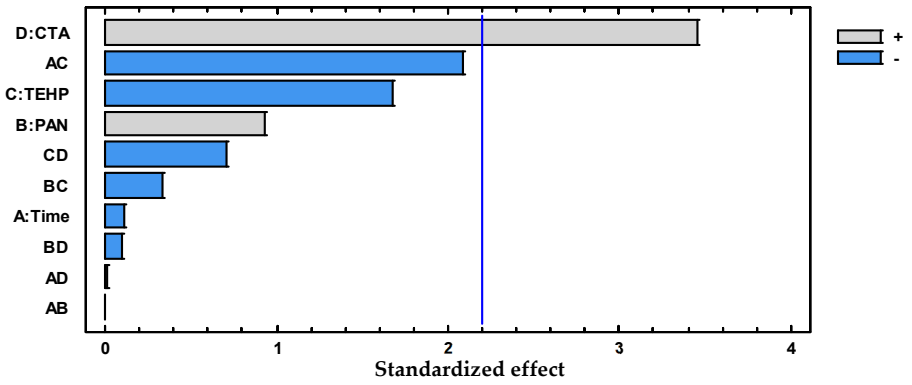


Figure S29. Pareto of the multivariate analysis performed with the M3 process method for the system PAN – Hg(II).

Table S23. ANOVA values of the multivariate analysis performed with the M3 process method for the system PAN – Hg(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,0000640569	1	0,0000640569	0,01	0,9152
B:PAN	0,00466858	1	0,00466858	0,87	0,3721
C:THEP	0,015153	1	0,015153	2,81	0,1218
D:CTA	0,0645229	1	0,0645229	11,97	**0,0053**
AB	0,0	1	0,0	0,00	1,0000
AC	0,0235508	1	0,0235508	4,37	0,0607
AD	2,76877E-7	1	2,76877E-7	0,00	0,9944
BC	0,000611178	1	0,000611178	0,11	0,7427
BD	0,0000548522	1	0,0000548522	0,01	0,9215
CD	0,00267146	1	0,00267146	0,50	0,4961
Total Error	0,0593142	11	0,0053922		
Total (corrected)	0,174981	21			
R^2	66.1025 %				
Adj - R^2	35,2867 %				
Standard error	0,0734316				
Std. Dev	0,0479888				

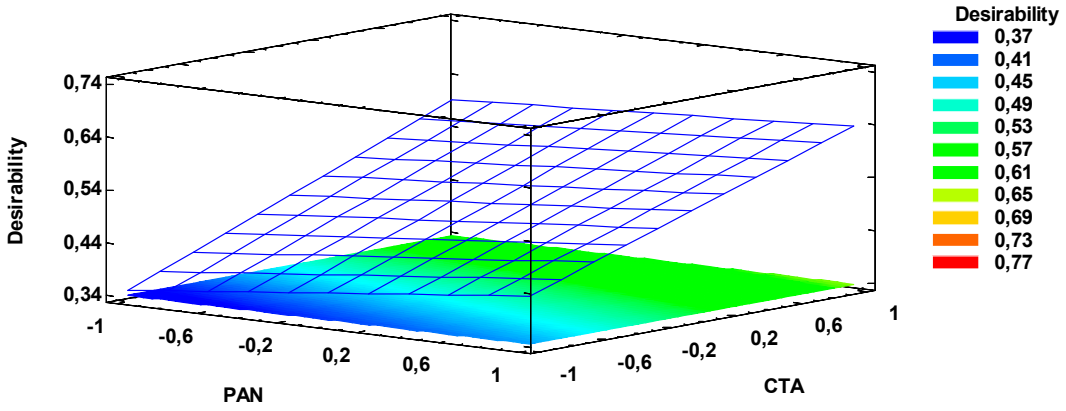


Figure S30. Response surface and contour plots of the multivariate analysis performed with the M3 process method for the system PAN– Hg(II), when THEP = Time = 0,0.

For the system PAN – Hg(II) the model was:

$$D = 0.503524 + 0.113536*CTA \quad (S17)$$

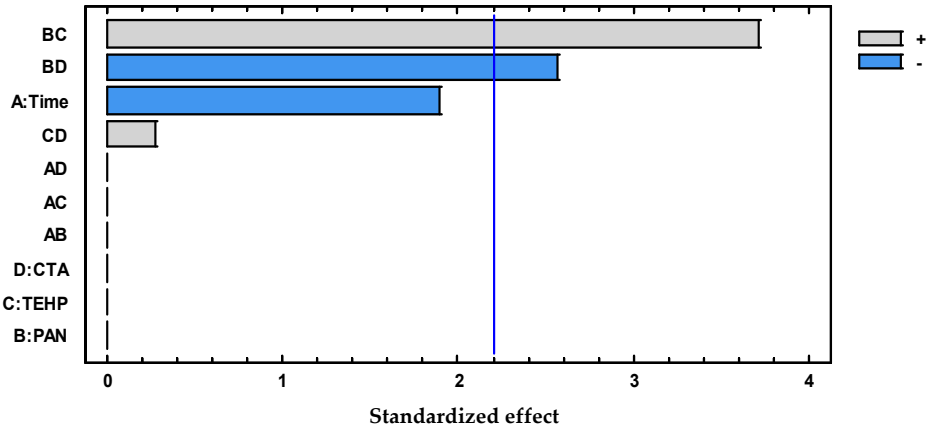


Figure S31. Pareto of the multivariate analysis performed with the M3 process method for the system PAN – Pb(II).

Table S24. ANOVA values of the multivariate analysis performed with the M3 process method for the system PAN – Pb(II).

Source	*Sum of squares*	*Df*	*Mean square*	*F-Ratio*	*P-Value*
A:Time	0,0409743	1	0,0409743	3,60	0,0844
B:PAN	0,0	1	0,0	0,00	1,0000
C:THEP	0,0	1	0,0	0,00	1,0000
D:CTA	0,0	1	0,0	0,00	1,0000
AB	0,0	1	0,0	0,00	1,0000
AC	0,0	1	0,0	0,00	1,0000
AD	0,0	1	0,0	0,00	1,0000
BC	0,157157	1	0,157157	13,80	**0,0034**
BD	0,0751327	1	0,0751327	6,60	**0,0261**
CD	0,000909381	1	0,000909381	0,08	0,7827
Total Error	0,125266	11	0,0113878		
Total (corrected)	0,357986	21			
R^2	65,0082 %				
Adj - R^2	33,1974 %				
Standard error	0,106714				

Std. Dev	0,0468218

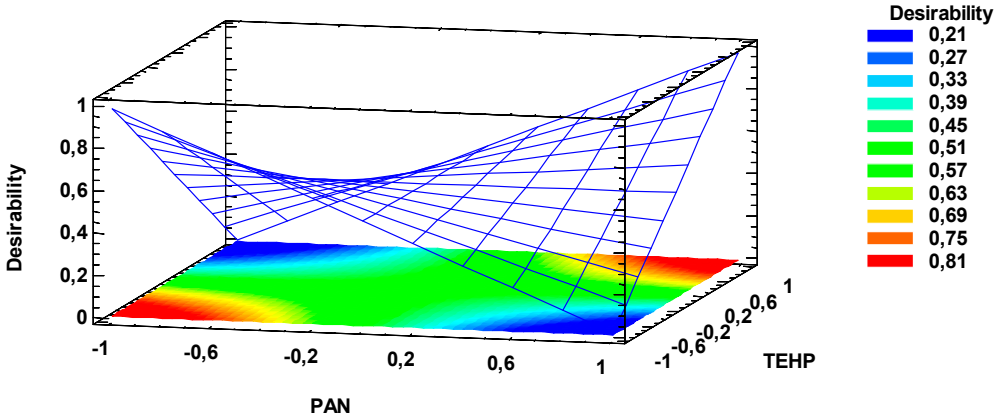


Figure S32. Response surface and contour plots of the multivariate analysis performed with the M3 process method for the system PAN – Pb(II), when CTA = Time = 0,0.

For the system PAN – Pb(II) the model was:

D = 0.494014 - + 0.48524*PAN*TEHP - 0.357177*PAN*CTA (S18)