Electronic Tongue for Simultaneous Determination of Cyanide, Thiocyanate and Iodide

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Abstract

Five cross selective electrodes comprising cyanide, thiocyanate, and iodide coated graphite electrodes CGEs were used as sensing parts of an electronic tongue for simultaneous determination of cyanide, thiocyanate, and iodide ions in the presence and the absence of chloride ion as a coexisting ion. The CGEs were constructed using poly(vinyl chloride) (PVC), o-nitrophenyl octyl ether (o-NPOE), cetyltrimethylammonium bromide (CTAB), and metal-porphyrin complexes as ionophores. The constructed electrodes were characterized to obtain their calibration curve, response time, and repeatability.

A programmed switching system combined with an array of the five potentiometric coated graphite electrodes (i.e., ion-selective or cross-selective electrodes) were connected directly to a pH/potentiometer and a computer to sequentially acquire the potential corresponding to water sample mixtures. The

acquired potentials were recorded and saved on the computer and were used as input variables for an artificial neural network to simultaneously yield the concentrations of cyanide, thiocyanate and iodide ions in simple and complex mixtures. A feed-forward, back propagation network with a Levenburg–Maquart algorithm was employed to optimize the network parameters.

Key words: Electronic Tongue; Cyanide; Thiocyanate; Iodide; Artificial Neural Network

1. Introduction

One of the most advantageous features of potentiometric sensors is their fast response that makes them convenient tools in the analysis of large number of samples. However, the cross selectivity of most of them sacrifice these characteristics, and make their use in complicated matrices difficult to some extent. As discussed in our previous work [1], application of some array of cross selective electrodes or the electrodes with low selectivity can compensate this failure.

Cyanide occurs naturally in many foods (e.g., cassava, flax, sorghum, bamboo shoots, and bitter almonds) and is naturally generated by microorganisms (fungi, algae, and bacteria) [2]. The ISE methods for cyanide ion are subject to interferences from iodide, sulfide, bromide, thiosulfate, and thiocyanate, and they are also matrix dependent [3-5].

Thiocyanate and iodide are two of the most lipophilic anions which can penetrate into the PVC membrane, so that the membranes may show considerable potential responses toward them even if no ionophore is added into the membranes. These characteristics may be vital if the

applied ionophores were not selective enough to the primary ion, so this makes the potentiometric sensors be cross-selective.

Determination of anions such as cyanide and thiocyanate in the presence of iodide may be necessary in clinical studies, as they can be found in biological samples. For example, thiocyanate contents may be found in the presence of cyanide ion in biological fluids of smokers or other poisoned with cyanide ion [6, 7]. On the other hand, iodide ion is also one of the nutrients needed for the endocrine gland, thyroid, to work properly [8]. Thus, the determination of iodide together with cyanide and thiocyanate in the biological sample is important. So, the simultaneous determination of cyanide, thiocyanate, and iodide ions was aimed in this work.

2. Experimental

2.1. Reagents and materials

Sodium or potassium salts of anions were purchased from Fluka or Merck, and were used without any further purification. High molecular weight PVC was prepared from Merck. All plasticizers were purchased from Fluka and used thoroughly. Metal-Schiff base and metal-porphyrin complexes were synthesized, and purified by using the procedure discussed in references [9, 10].

2.2. Electronic Tongue configuration

A five ion-selective-electrode-array system was employed for obtaining potential of the samples containing the anionic species. The home-made instrument was used to acquire the potentials, sequentially (Fig. 1) [1]. In the current study, just five ports of the system were turned on. Thus in this case, the potential acquisition time was expected to reduced, compared to the previous

work, associated with the use of seven sensors. However, in the current study, it was tried to use cross selective electrodes which could contain information corresponding to all of the anionic species.

Fig. 1

2.3. Electrode preparation

The membrane-coated graphite electrodes were prepared using the procedure discussed in the literature [1]. The optimized membrane compositions of the electrodes are summarized in Table 1. As it is seen, the electrodes nos. 1 and 4 are cyanide selective electrodes, electrodes nos. 2 and 3 are thiocyanate selective, and electrode no. 5 is an iodide selective electrode [9]. The electrodes were conditioned in the solutions of ions of interest for at least 48 h.

2.4. Sample preparation

45 ternary sample mixtures of the anions with random concentrations of cyanide in the range of 1.0×10^{-2} M to 3.0×10^{-5} M, thiocyanate, and iodide in the range of 1.0×10^{-2} M to 1.0×10^{-5} M were prepared as calibration sample sets. Addition of some buffering solution was necessary to adjust pH of each of the samples in a proper pH, the hydrolysis of cyanide and thiocyanate being neglected. The optimized pH range for the two membrane coated graphite electrodes were 4.2-9.3 and 4.4-9.6 for thiocyanate selective electrodes. It was 9.5 for both cyanide selective electrodes and was about 2.0-9.5 for the iodide selective electrode. Consequently, all of the applied samples were buffered at a constant pH of 9.3, as all of the electrodes work conveniently at this pH, and the interference from OH^- ion in this region is also tolerable. Thus, 5 mL of borax buffer (0.1 M of pH 9.3) was added to each of sample solutions. After that, proper amounts of stock sodium cyanide, sodium thiocyanate, and sodium iodide solutions were added consecutively to the samples to obtain different random concentrations of the aforementioned anions. Finally, the samples were diluted to 25 mL; so, all of the samples had approximately a constant ionic strength.

In order to evaluate the analytical application of the array system, a set of 10 samples with different concentration of the aforementioned anions were made (Table 2). To check the reliability of the array configuration for predicting the anion concentrations, another 11 sample sets was also prepared with different random concentration of the anions in the presence of different concentration levels of chloride ion with a similar procedure discussed above (Table 3).

Table 1. Composition of the coated graphite ion selective electrodes and their response times R.T

(s); A-E, represent ionophores as shown at the beneath of the Table

Electrode no.	Ionophore Structure	Composition(%)				R.T.	R.T. in
		Ionophore	Plasticizer	PVC	Additive	Alone	Array
1. CN^- -ISE	A	1.2	65.5(o-NPOE)	32.7	0.6(CTAB)	6	8
2. SCN^- -ISE	B	1.0	65.5(o-NPOE)	32.7	0.8(CTAB)	5	7
3. SCN^- -ISE	C	1.0	65.7(o-NPOE)	32.8	0.5(CTAB)	6	8
4. CN^- -ISE	D	0.8	65.5(o-NPOE)	32.7	1.0(CTAB)	5	6
5. I^- -ISE	E	1.5	69.5(o-NPOE)	28.0	1.0(TBAB)	6	7

A

B

C

D

E

Table 2. Prediction sample sets in the absence of chloride ion

Sample no.	SCN ⁻ (M)	CN ⁻ (M)	I ⁻ (M)
1	9.0×10^{-5}	5.4×10^{-3}	1.0×10^{-3}
2	5.0×10^{-3}	2.0×10^{-3}	7.0×10^{-4}
3	3.0×10^{-4}	7.0×10^{-3}	3.0×10^{-3}
4	1.0×10^{-5}	3.0×10^{-4}	2.0×10^{-3}
5	2.0×10^{-3}	1.0×10^{-4}	3.0×10^{-5}
6	3.0×10^{-3}	2.0×10^{-3}	6.0×10^{-3}
7	5.0×10^{-4}	4.0×10^{-4}	4.0×10^{-4}
8	1.0×10^{-2}	3.0×10^{-3}	3.0×10^{-3}
9	8.0×10^{-4}	5.0×10^{-4}	5.0×10^{-5}
10	4.0×10^{-4}	3.0×10^{-5}	7.0×10^{-3}

3. Results and discussion

3.1. Response time study

As mentioned earlier, sample matrices have such an intensive effect on the response of each electrode. So it was necessary to evaluate and average response time of each electrode in the mixtures. To do so, a solution containing 1.0×10^{-3} M of all the ions under study, except the one that its response time is going to be determined, was used. Then concentration of the primary ion of the electrode under study was changed from 1.0×10^{-6} M to 1.0×10^{-2} M. As mentioned earlier, these response times might be different from the case where the electrodes used alone.

Table 3. Prediction sample sets in the presence of chloride ion

Sample no.	SCN ⁻ (M)	CN ⁻ (M)	I ⁻ (M)	Cl ⁻ (M)
1	2.0×10 ⁻³	5.0×10 ⁻⁴	5.0×10 ⁻³	2.0×10 ⁻³
2	4.0×10 ⁻⁴	2.0×10 ⁻³	7.0×10 ⁻³	1.0×10 ⁻³
3	2.0×10 ⁻⁵	1.0×10 ⁻²	3.0×10 ⁻⁴	1.0×10 ⁻²
4	1.0×10 ⁻²	6.0×10 ⁻⁴	2.0×10 ⁻³	1.0×10 ⁻¹
5	5.0×10 ⁻⁴	1.0×10 ⁻²	4.0×10 ⁻⁴	1.0×10 ⁻³
6	3.0×10 ⁻³	5.0×10 ⁻⁴	2.0×10 ⁻³	3.0×10 ⁻³
7	3.0×10 ⁻³	2.0×10 ⁻³	6.0×10 ⁻³	1.0×10 ⁻³
8	5.0×10 ⁻⁴	4.0×10 ⁻⁴	4.0×10 ⁻⁴	8.0×10 ⁻⁴
9	1.0×10 ⁻²	3.0×10 ⁻³	3.0×10 ⁻³	2.0×10 ⁻²
10	8.0×10 ⁻⁴	5.0×10 ⁻⁴	5.0×10 ⁻⁵	2.0×10 ⁻²
11	4.0×10 ⁻⁴	8.0×10 ⁻⁵	7.0×10 ⁻³	3.0×10 ⁻³

3.2. Selectivity coefficient measurements

The selectivity coefficients of the electrodes were measured using fixed interference method (FIM) and the resulting data were summarized in Table 4. As it is seen, electrodes no. 1, and 2, respond selectively towards SCN⁻ and CN⁻, respectively, while electrodes no. 3 and 4 have shown less selectivity (cross selectivity) towards these anions. It is interesting to note that these selectivity data might be different from the results obtained for each electrode alone. This is because when the electrodes are used in the array configuration, a bias initiated from the home-made instrument may affect the selectivity coefficient values [11].

Table 4. Selectivity coefficient measurements for the electrodes in the array system

A^{n-}	$\log K_{CN,j}^{pot,FIM}$	$\log K_{SCN,j}^{pot,FIM}$	$\log K_{SCN,j}^{pot,FIM}$	$\log K_{CN,j}^{pot,FIM}$	$\log K_{I,j}^{pot,FIM}$
SCN^-	-2.41	0.0	0.0	-2.41	-1.83
CN^-	0.0	-1.73	-2.39	0.0	-1.65
Cl^-	-3.41	-3.64	-3.13	-3.61	-4.01
F^-	-3.42	-4.23	-3.95	-4.33	-4.86
Br^-	-3.21	-3.55	-3.31	-3.72	-3.35
I^-	-3.15	-3.11	-3.21	-2.91	0.0
SO_4^{2-}	<-5	<-5	<-5	<-5	<-5
NO_3^-	<-5	<-5	<-5	<-5	<-5
CH_3COO^-	-3.36	-3.92	-3.60	-3.15	<-5
S^{2-}	-2.62	-3.22	-2.27	-2.43	-3.61
HPO_4^{2-}	-3.01	-4.13	-2.91	-3.01	-2.97
CO_3^{2-}	-3.21	-3.13	-2.16	-3.31	-3.52
$C_2O_4^{2-}$	-3.02	-2.31	-2.82	-2.99	-3.31
N_3^-	-3.14	-3.25	-3.10	-2.98	-3.45

3.3.Array optimization, artificial neural network

To optimize the array configuration, artificial neural network was applied using back propagation neural network toolbox available in MATLAB software version 7.5.0.342 [12-13].

Each electrode's response toward concentrations of different constituents in the calibration samples were used to construct a model for predicting the concentration of the different anions.

A neural network with three hidden layers having 4, 3, and 3 nodes was created and trained to simulate the electrodes responses to each of the calibration and prediction samples. It is important to note that autoscaling of the potential data is required. So the potential matrices of calibration and prediction samples were autoscaled with a program in MATLAB prior to feeding the potentials to the network.

The squared correlation coefficient, R^2 , values were measured and summarized in Tables 5-7 in each step of optimization as mentioned before, so that the R^2 values were then used as a measure of goodness of fit, to obtain the proper combination of the electrode by which the concentration of the anions with a minimum analysis time and improved accuracy and precision can be predicted simultaneously (Table 5).

As R^2 values indicate, electrodes no. 1 and 2 showed good predictability towards SCN^- , but they were unable to precisely predict either CN^- or I^- concentrations. Electrodes nos. 2 and 3 have shown similar behaviors towards CN^- , but they were unable to predict either SCN^- or I^- concentrations. Electrode no 5 was just suitable for predicting concentrations of iodide ion. As it is concluded from the correlation coefficients in Table 5, the electrode no. 5 is the only electrode by which the concentration of iodide ion can be predicted. On the other hand, the concentration of cyanide ion can be found by each of the electrodes nos. 1 and 4. The electrodes nos. 2 and 3 just could predict concentration of thiocyanate ion in both calibration and prediction sample sets.

Table 5. Optimization of the array

Array	Target ion ^a	R ² -Training	R ² -Prediction ^b
{1} ^c	SCN ⁻	0.3639	0.0032
{1}	CN ⁻	0.8188	0.9760
{1}	I ⁻	0.0274	0.2248
{2}	SCN ⁻	0.9739	0.9955
{2}	CN ⁻	0.0049	0.0222
{2}	I ⁻	0.0000	0.1004
{3}	SCN ⁻	0.9876	0.9552
{3}	CN ⁻	0.3561	0.1476
{3}	I ⁻	0.0526	0.0000
{4}	SCN ⁻	0.0134	0.0547
{4}	CN ⁻	0.9882	0.8807
{4}	I ⁻	0.0023	0.1128
{5}	SCN ⁻	0.0647	0.1226
{5}	CN ⁻	0.0456	0.5948
{5}	I ⁻	0.9713	0.9686

^a Target ion is an ion by which the array is modeled to predict its concentration.

^b Prediction sample sets in Table 2 are used.

^c The number in { } is the electrode number employed in the array.

Having these conclusions in mind, it was tried to assess the combinations of the proper and the improper electrodes shown in Table 6 to find the best array configuration by which the analysis

time is minimized while the accuracy and precision is maximized (Table 7). As it can be seen from Table 7, a combination of one proper electrode with an improper one (i. e. electrodes nos. 1 and 2), resulted in a better prediction for both cyanide and thiocyanate ions compared to the results shown in Table 5, but it is not suitable for predicting iodide ion concentration. Improvement of the predictability of {1, 2} array compared to that of electrode no. 1 or 2 alone may be probably due to the cross selectivity of the electrodes no. 1 in one hand, and lipophilicity of thiocyanate ion on the other hand, which results in the response of both of the membrane electrodes towards it. As a result, excellent squared correlation coefficients of 0.9998 and 0.9994 were obtained for the calibration and the prediction sets, respectively. Entering electrode no. 5 in {1, 2} array resulted in a better prediction of iodide ion, but the prediction for both cyanide and thiocyanate got worse, since the presence of electrode no. 5 is necessary for predicting iodide ion concentration. Other combinations of the proper and the improper electrodes were tested.

Table 6. Evaluation of the electrodes in the array

Proper electrode no.	Improper electrode no.
2	1
4	3 (not so improper)
5	-

Table 7. Correlation coefficients for combination of the electrodes in array

Array	Target ion	R ² -Training	R ² -Prediction
{1, 2} ^a	SCN ⁻	0.9998	0.9994
{1, 2}	CN ⁻	0.9998	0.9326
{1, 2}	I ⁻	0.0150	0.0501
{1, 2, 5}	SCN ⁻	0.8855	0.9662
{1, 2, 5}	CN ⁻	0.6470	0.9054
{1, 2, 5}	I ⁻	0.9189	0.9437
{2, 3, 5}	SCN ⁻	0.9909	0.9780
{2, 3, 5}	CN ⁻	0.7074	0.7825
{2, 3, 5}	I ⁻	0.9477	0.9245
{2, 4, 5}	SCN ⁻	0.9595	0.9882
{2, 4, 5}	CN ⁻	0.9823	0.9735
{2, 4, 5}	I ⁻	0.9522	0.9832
{1, 2, 4, 5}	SCN ⁻	0.9992	0.9852
{1, 2, 4, 5}	CN ⁻	0.9797	0.9807
{1, 2, 4, 5}	I ⁻	0.9514	0.9245
{2 -5}	SCN ⁻	0.9967	0.9776
{2 -5}	CN ⁻	0.9922	0.9464
{2-5}	I ⁻	0.9743	0.9198
{1-5}	SCN ⁻	0.9980	0.9857
{1-5}	CN ⁻	0.9944	0.8297
{1- 5}	I ⁻	0.9924	0.6661

^a The number(s) in { } is the electrode number employed in the array.

As the results show, the best predictions were obtained with array {2, 4, 5}, as a combination of proper electrodes (Table 6). Entering the other electrodes either proper or improper ones, not only resulted in a worse prediction, but also resulted in prolonged analysis time. Thus it was decided to choose this electrode combination for further analysis of the samples.

It is worth mentioning that the electrodes nos. 2, 4, and 5 are all constructed based on the metal-prophyrin derivatives, and the other electrodes were constructed based on the metal-Schiff base complexes. These results show the superiority of the metal-porphyrin derivatives for construction of anion selective electrodes, as several literatures reported the use of these compounds as suitable ionophores for constructing some anion selective electrodes [9, 15-21]. The electronic tongue was successfully applied for prediction of the anions in the absence and presence of a foreign ion such as chloride ion. The results were summarized in Tables 8 and 9. Correlation plot corresponding to each ion was depicted in Fig. 2 and Fig. 3. As correlation plots indicate, prediction capability of the system was not changed significantly in the presence of the foreign ion which it coexist in a higher concentration compared to the primary ion concentration.

Table 8. Prediction of the anions concentration in the absence of interfering ion

Sample no.	Actual concentration (M)			Predicted concentration (M)		
	SCN ⁻	CN ⁻	I ⁻	SCN ⁻	CN ⁻	I ⁻
1	9.0×10^{-5}	5.4×10^{-3}	1.0×10^{-3}	6.7×10^{-5}	5.7×10^{-3}	1.1×10^{-3}
2	5.0×10^{-3}	2.0×10^{-3}	7.0×10^{-4}	5.2×10^{-3}	2.0×10^{-3}	6.0×10^{-4}
3	3.0×10^{-4}	7.0×10^{-3}	3.0×10^{-3}	4.0×10^{-4}	8.0×10^{-3}	3.4×10^{-3}
4	1.0×10^{-5}	3.0×10^{-4}	2.0×10^{-3}	8.1×10^{-6}	3.1×10^{-4}	1.8×10^{-3}
5	2.0×10^{-3}	1.0×10^{-4}	3.0×10^{-5}	3.2×10^{-3}	1.4×10^{-4}	4.7×10^{-4}
6	3.0×10^{-3}	2.0×10^{-3}	6.0×10^{-3}	3.5×10^{-3}	2.7×10^{-3}	5.3×10^{-3}
7	5.0×10^{-4}	4.0×10^{-4}	4.0×10^{-4}	3.8×10^{-4}	4.9×10^{-4}	8.9×10^{-4}
8	1.0×10^{-2}	3.0×10^{-3}	3.0×10^{-3}	1.1×10^{-2}	4.6×10^{-3}	2.7×10^{-3}
9	8.0×10^{-4}	5.0×10^{-4}	5.0×10^{-5}	1.3×10^{-4}	6.9×10^{-4}	2.2×10^{-4}
10	4.0×10^{-4}	3.0×10^{-5}	7.0×10^{-3}	3.6×10^{-4}	7.0×10^{-6}	7.0×10^{-3}

Table 9. Prediction of the anions concentration in the presence of interfering ion

Sample no.	Actual concentrations (M)				Predicted concentrations (M)		
	SCN ⁻	CN ⁻	I ⁻	Cl ⁻	SCN ⁻	CN ⁻	I ⁻
1	2.0×10^{-3}	5.0×10^{-4}	5.0×10^{-3}	2.0×10^{-3}	1.7×10^{-3}	1.0×10^{-3}	4.5×10^{-3}
2	4.0×10^{-4}	2.0×10^{-3}	7.0×10^{-3}	1.0×10^{-3}	5.7×10^{-4}	2.3×10^{-3}	6.1×10^{-3}
3	2.0×10^{-5}	1.0×10^{-2}	3.0×10^{-4}	1.0×10^{-2}	4.4×10^{-6}	1.4×10^{-2}	1.3×10^{-4}
4	1.0×10^{-2}	6.0×10^{-4}	2.0×10^{-3}	1.0×10^{-1}	1.1×10^{-2}	7.0×10^{-4}	2.1×10^{-3}
5	5.0×10^{-4}	1.0×10^{-2}	4.0×10^{-4}	1.0×10^{-3}	3.1×10^{-4}	9.8×10^{-3}	1.2×10^{-4}
6	3.0×10^{-3}	5.0×10^{-4}	2.0×10^{-3}	3.0×10^{-3}	2.3×10^{-3}	4.0×10^{-4}	2.9×10^{-3}
7	3.0×10^{-3}	2.0×10^{-3}	6.0×10^{-3}	1.0×10^{-3}	4.1×10^{-3}	2.6×10^{-3}	5.2×10^{-3}
8	5.0×10^{-4}	4.0×10^{-4}	4.0×10^{-4}	8.0×10^{-4}	3.8×10^{-4}	4.9×10^{-4}	8.9×10^{-4}
9	1.0×10^{-2}	3.0×10^{-3}	3.0×10^{-3}	2.0×10^{-2}	1.1×10^{-2}	4.8×10^{-3}	2.7×10^{-3}
10	8.0×10^{-4}	5.0×10^{-4}	5.0×10^{-5}	2.0×10^{-2}	1.3×10^{-3}	6.9×10^{-4}	2.2×10^{-4}
11	4.0×10^{-4}	8.0×10^{-5}	7.0×10^{-3}	3.0×10^{-3}	3.6×10^{-4}	4.5×10^{-5}	6.6×10^{-3}

Fig. 2

Fig. 3

4. Conclusion

An array of anion selective electrodes comprising an iodide-ion selective electrode, two cyanide-ion selective electrodes, and two thiocyanate-ion selective electrodes were tested for simultaneous determination of thiocyanate, cyanide and iodide ions in the absence and presence of the different concentration levels of chloride ion as a coexisting ion. Each of the electrodes mentioned, especially cyanide and thiocyanate-ion selective electrodes based on metal-Schiff base complexes were cross selective towards lipophilic anions such as thiocyanate or iodide. However, it causes improvement of accuracy of prediction of the array system, as the arrays comprising these electrodes have shown a better predictability towards the anions compared to the case where these electrodes were used alone. Metal-porphyrin complex derivatives were found as better ion carriers than metal-Schiff base complexes in construction of array system, as the constructed electrodes based on these carriers showed the best accuracy for the analytes. The most important benefit of using such a system is its short analysis time compared to the case where each sample was assayed for its content using just one ion selective electrode, without sacrificing the accuracy of such an array for predicting all of the anions, simultaneously. This accuracy is comparable to the case where each electrode was used alone, as it is shown from the data.

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5. References

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Caption of Figures

Fig. 1. Manifold of the Electronic Tongue, Sample (1); Arrays of Sensors (2); Reference

electrode (3); Switching system (4); pH Meter (5); Output of the switching system (Input to the pH Meter) (6); computer (7); Serial connection of pH meter to computer (8); Serial connection of the switching system to computer (9)

Fig. 2. Correlation plots for determination of anions in the sample sets of Table 2

Fig. 3. Correlation plots for determination of anions in the sample sets of Table 3

Caption of Tables

Table 1. Composition of the coated graphite ion selective electrodes and their response times R.T

(s); A-E, represent ionophores as shown at the beneath of the Table

Table 2. . Prediction sample sets in the absence of chloride ion

Table 3. Prediction sample sets in the presence of chloride ion

Table 4. Selectivity coefficient measurements for the electrodes in the array system

Table 5. Optimization of the array configuration

Table 6. Evaluation of the electrodes in the array

Table 7. Correlation coefficients for combination of the electrodes in array

Table 8. Prediction of the anions concentration in the absence of interfering ion

Table 9. Prediction of the anions concentration in the presence of interfering ion

Fig. 1

Fig. 2

Fig. 3

Table 1

Electrode no.	Ionophore	Composition(%)				R.T.	R.T. in
	Structure					Alone	Array
		Ionophore	Plasticizer	PVC	Additive		
1. CN^- -ISE	A	1.2	65.5(o-NPOE)	32.7	0.6(CTAB)	6	8
2. SCN^- -ISE	B	1.0	65.5(o-NPOE)	32.7	0.8(CTAB)	5	7
3. SCN^- -ISE	C	1.0	65.7(o-NPOE)	32.8	0.5(CTAB)	6	8
4. CN^- -ISE	D	0.8	65.5(o-NPOE)	32.7	1.0(CTAB)	5	6
5. I^- -ISE	E	1.5	69.5(o-NPOE)	28.0	1.0(TBAB)	6	7

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Table 2

Sample no.	SCN ⁻ (M)	CN ⁻ (M)	I ⁻ (M)
1	9.0×10^{-5}	5.4×10^{-3}	1.0×10^{-3}
2	5.0×10^{-3}	2.0×10^{-3}	7.0×10^{-4}
3	3.0×10^{-4}	7.0×10^{-3}	3.0×10^{-3}
4	1.0×10^{-5}	3.0×10^{-4}	2.0×10^{-3}
5	2.0×10^{-3}	1.0×10^{-4}	3.0×10^{-5}
6	3.0×10^{-3}	2.0×10^{-3}	6.0×10^{-3}
7	5.0×10^{-4}	4.0×10^{-4}	4.0×10^{-4}
8	1.0×10^{-2}	3.0×10^{-3}	3.0×10^{-3}
9	8.0×10^{-4}	5.0×10^{-4}	5.0×10^{-5}
10	4.0×10^{-4}	3.0×10^{-5}	7.0×10^{-3}

Table 3

Sample no.	SCN ⁻ (M)	CN ⁻ (M)	I ⁻ (M)	Cl ⁻ (M)
1	2.0×10 ⁻³	5.0×10 ⁻⁴	5.0×10 ⁻³	2.0×10 ⁻³
2	4.0×10 ⁻⁴	2.0×10 ⁻³	7.0×10 ⁻³	1.0×10 ⁻³
3	2.0×10 ⁻⁵	1.0×10 ⁻²	3.0×10 ⁻⁴	1.0×10 ⁻²
4	1.0×10 ⁻²	6.0×10 ⁻⁴	2.0×10 ⁻³	1.0×10 ⁻¹
5	5.0×10 ⁻⁴	1.0×10 ⁻²	4.0×10 ⁻⁴	1.0×10 ⁻³
6	3.0×10 ⁻³	5.0×10 ⁻⁴	2.0×10 ⁻³	3.0×10 ⁻³
7	3.0×10 ⁻³	2.0×10 ⁻³	6.0×10 ⁻³	1.0×10 ⁻³
8	5.0×10 ⁻⁴	4.0×10 ⁻⁴	4.0×10 ⁻⁴	8.0×10 ⁻⁴
9	1.0×10 ⁻²	3.0×10 ⁻³	3.0×10 ⁻³	2.0×10 ⁻²
10	8.0×10 ⁻⁴	5.0×10 ⁻⁴	5.0×10 ⁻⁵	2.0×10 ⁻²
11	4.0×10 ⁻⁴	8.0×10 ⁻⁵	7.0×10 ⁻³	3.0×10 ⁻³

Table 4

A^{n-}	$\log K_{CN,j}^{pot,FIM}$	$\log K_{SCN,j}^{pot,FIM}$	$\log K_{SCN,j}^{pot,FIM}$	$\log K_{CN,j}^{pot,FIM}$	$\log K_{I,j}^{pot,FIM}$
SCN^-	-2.41	0.0	0.0	-2.41	-1.83
CN^-	0.0	-1.73	-2.39	0.0	-1.65
Cl^-	-3.41	-3.64	-3.13	-3.61	-4.01
F^-	-3.42	-4.23	-3.95	-4.33	-4.86
Br^-	-3.21	-3.55	-3.31	-3.72	-3.35
I^-	-3.15	-3.11	-3.21	-2.91	0.0
SO_4^{2-}	<-5	<-5	<-5	<-5	<-5
NO_3^-	<-5	<-5	<-5	<-5	<-5
CH_3COO^-	-3.36	-3.92	-3.60	-3.15	<-5
S^{2-}	-2.62	-3.22	-2.27	-2.43	-3.61
HPO_4^{2-}	-3.01	-4.13	-2.91	-3.01	-2.97
CO_3^{2-}	-3.21	-3.13	-2.16	-3.31	-3.52
$C_2O_4^{2-}$	-3.02	-2.31	-2.82	-2.99	-3.31
N_3^-	-3.14	-3.25	-3.10	-2.98	-3.45

Table 5

Array	Target ion ^a	R ² -Training	R ² -Prediction ^b
{1} ^c	SCN ⁻	0.3639	0.0032
{1}	CN ⁻	0.8188	0.9760
{1}	I ⁻	0.0274	0.2248
{2}	SCN ⁻	0.9739	0.9955
{2}	CN ⁻	0.0049	0.0222
{2}	I ⁻	0.0000	0.1004
{3}	SCN ⁻	0.9876	0.9552
{3}	CN ⁻	0.3561	0.1476
{3}	I ⁻	0.0526	0.0000
{4}	SCN ⁻	0.0134	0.0547
{4}	CN ⁻	0.9882	0.8807
{4}	I ⁻	0.0023	0.1128
{5}	SCN ⁻	0.0647	0.1226
{5}	CN ⁻	0.0456	0.5948
{5}	I ⁻	0.9713	0.9686

^a Target ion is an ion by which the array is modeled to predict its concentration.

^b Prediction sample sets in Table 2 are used.

^c The number in { } is the electrode number employed in the array.

Table 6

Proper electrode no.	Improper electrode no.
2	1
4	3 (not so improper)
5	-

Table 7

Array	Target ion	R ² -Training	R ² -Prediction
{1, 2} ^a	SCN ⁻	0.9998	0.9994
{1, 2}	CN ⁻	0.9998	0.9326
{1, 2}	I ⁻	0.0150	0.0501
{1, 2, 5}	SCN ⁻	0.8855	0.9662
{1, 2, 5}	CN ⁻	0.6470	0.9054
{1, 2, 5}	I ⁻	0.9189	0.9437
{2, 3, 5}	SCN ⁻	0.9909	0.9780
{2, 3, 5}	CN ⁻	0.7074	0.7825
{2, 3, 5}	I ⁻	0.9477	0.9245
{2, 4, 5}	SCN ⁻	0.9595	0.9882
{2, 4, 5}	CN ⁻	0.9823	0.9735
{2, 4, 5}	I ⁻	0.9522	0.9832
{1, 2, 4, 5}	SCN ⁻	0.9992	0.9852
{1, 2, 4, 5}	CN ⁻	0.9797	0.9807
{1, 2, 4 5}	I ⁻	0.9514	0.9245
{2 -5}	SCN ⁻	0.9967	0.9776
{2 -5}	CN ⁻	0.9922	0.9464
{2-5}	I ⁻	0.9743	0.9198
{1-5}	SCN ⁻	0.9980	0.9857
{1-5}	CN ⁻	0.9944	0.8297
{1- 5}	I ⁻	0.9924	0.6661

^a The number(s) in { } is the electrode number employed in the array.

Table 8

Sample no.	Actual concentration (M)			Predicted concentration (M)		
	SCN ⁻	CN ⁻	I ⁻	SCN ⁻	CN ⁻	I ⁻
1	9.0×10 ⁻⁵	5.4×10 ⁻³	1.0×10 ⁻³	6.7×10 ⁻⁵	5.7×10 ⁻³	1.1×10 ⁻³
2	5.0×10 ⁻³	2.0×10 ⁻³	7.0×10 ⁻⁴	5.2×10 ⁻³	2.0×10 ⁻³	6.0×10 ⁻⁴
3	3.0×10 ⁻⁴	7.0×10 ⁻³	3.0×10 ⁻³	4.0×10 ⁻⁴	8.0×10 ⁻³	3.4×10 ⁻³
4	1.0×10 ⁻⁵	3.0×10 ⁻⁴	2.0×10 ⁻³	8.1×10 ⁻⁵	3.1×10 ⁻⁴	1.8×10 ⁻³
5	2.0×10 ⁻³	1.0×10 ⁻⁴	3.0×10 ⁻⁵	3.2×10 ⁻³	1.4×10 ⁻⁴	4.7×10 ⁻⁴
6	3.0×10 ⁻³	2.0×10 ⁻³	6.0×10 ⁻³	3.5×10 ⁻³	2.7×10 ⁻³	5.3×10 ⁻³
7	5.0×10 ⁻⁴	4.0×10 ⁻⁴	4.0×10 ⁻⁴	3.8×10 ⁻⁴	4.9×10 ⁻⁴	8.9×10 ⁻⁴
8	1.0×10 ⁻²	3.0×10 ⁻³	3.0×10 ⁻³	1.1×10 ⁻²	4.6×10 ⁻³	2.7×10 ⁻³
9	8.0×10 ⁻⁴	5.0×10 ⁻⁴	5.0×10 ⁻⁵	1.3×10 ⁻⁴	6.9×10 ⁻⁴	2.2×10 ⁻⁴
10	4.0×10 ⁻⁴	3.0×10 ⁻⁵	7.0×10 ⁻³	3.6×10 ⁻⁴	7.0×10 ⁻⁶	7.0×10 ⁻³

Table 9

Sample no.	Actual concentrations (M)				Predicted concentrations (M)		
	SCN ⁻	CN ⁻	I ⁻	Cl ⁻	SCN ⁻	CN ⁻	I ⁻
1	2.0×10^{-3}	5.0×10^{-4}	5.0×10^{-3}	2.0×10^{-3}	1.7×10^{-3}	1.0×10^{-3}	4.5×10^{-3}
2	4.0×10^{-4}	2.0×10^{-3}	7.0×10^{-3}	1.0×10^{-3}	5.7×10^{-4}	2.3×10^{-3}	6.1×10^{-3}
3	2.0×10^{-5}	1.0×10^{-2}	3.0×10^{-4}	1.0×10^{-2}	4.4×10^{-6}	1.4×10^{-2}	1.3×10^{-4}
4	1.0×10^{-2}	6.0×10^{-4}	2.0×10^{-3}	1.0×10^{-1}	1.1×10^{-2}	7.0×10^{-4}	2.1×10^{-3}
5	5.0×10^{-4}	1.0×10^{-2}	4.0×10^{-4}	1.0×10^{-3}	3.1×10^{-4}	9.8×10^{-3}	1.2×10^{-4}
6	3.0×10^{-3}	5.0×10^{-4}	2.0×10^{-3}	3.0×10^{-3}	2.3×10^{-3}	4.0×10^{-4}	2.9×10^{-3}
7	3.0×10^{-3}	2.0×10^{-3}	6.0×10^{-3}	1.0×10^{-3}	4.1×10^{-3}	2.6×10^{-3}	5.2×10^{-3}
8	5.0×10^{-4}	4.0×10^{-4}	4.0×10^{-4}	8.0×10^{-4}	3.8×10^{-4}	4.9×10^{-4}	8.9×10^{-4}
9	1.0×10^{-2}	3.0×10^{-3}	3.0×10^{-3}	2.0×10^{-2}	1.1×10^{-2}	4.8×10^{-3}	2.7×10^{-3}
10	8.0×10^{-4}	5.0×10^{-4}	5.0×10^{-5}	2.0×10^{-2}	1.3×10^{-3}	6.9×10^{-4}	2.2×10^{-4}
11	4.0×10^{-4}	8.0×10^{-5}	7.0×10^{-3}	3.0×10^{-3}	3.6×10^{-4}	4.5×10^{-5}	6.6×10^{-3}