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Novel Potentiometric Liquid Membrane Sensor for Chitosan Determination in Food Supplements

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A novel selective nano-chitosan liquid membrane sensor depends on the combination between chitosan and 2-(5-Bromo-2-Pyridylazo)-5-[N-n-Propyl-N-(3-sulfopropyl)amino]aniline reagent was successfully developed. The characteristics slope (54 mV/decade),linear range response from 1.0×10^{-7}-1.0×10^{-2} M, limit of detection(1.47×10^{-8}) M, selectivity study toward some inorganic cations, the time of response(10s), lifespan (five months), pH influence on the electrode potential and the crucial characteristic factors were studied. The electrode was successfully employed to estimate nano-chitosan in food supplements and fruit juice with nano-chitosan. The results obtained by the nominated sensor were analyzed, statistically treated and compared with the other recently described sensors.

Keywords: Ion-associate complexes, membrane sensor, nano-chitosan detection, food supplements.

1. INTRODUCTION

In recent years, chitosan (CHN) has attracted great and considerable attention as a prospect polysaccharide purse figure 1. It is a linear amino polysaccharide of glucosamine and N-acetyl glucosamine units and is produced from alkaline deacetylation of chitin[1]. The important specifications of chitosan increase its polymeric applications in agriculture, water treatment, food and textile industries [2 -5], pharmaceutical utilities [6] owing to their crucial characteristics to employ in the biomedical area, such as biodegradability, non-toxicity and biocompatibility.

However, it is needed to design such economic, sensitive, specific and quick systems, which can estimate CHN content, ion-selective membrane sensors as simple, fast, mobile, small, and low- cost apparatus can be used to detect chitosan[7-9].

Several traditional standard analytical techniques have been deployed for the detection of chitosan, CHN concentration includes colorimetric methods[10-14]. Thus, these techniques have some disadvantages of more expensive, complex pretreatment for samples, time-consuming, and tedious demands.

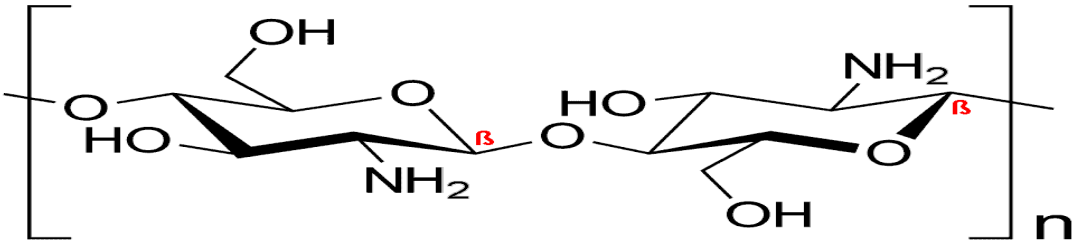

Figure 1. Chemical structure of nano-chitosan

However, there is an insistent necessity to set a new estimation technique to facilitate the CHN estimation, economic and more veracity. Recently, numerous researches are published as electrochemical selective electrodes for CHN determination[15-23]. Most of them concentrated on beneficent the sensitivity, stability, and other execution of the electrochemical applications. Sensors with simple condition, renewable easily and super stability can be employed as a new research trend.

The electrochemical applications are commonly interested about increasing researchers owing to its advantages of being simple, quick, economical, and can be employed to recognizes on-site inspection [24]. So, electrochemical strategies have been commonly applied in biological[25-30]and environmental analysis[31-32].

Despite the recently reported modes have high sensitivity and provide accurate and precise results, some problems were produced in their applications. Therefore, they are not applied for routine and on-site analysis. Potentiometric monitors depend on selective electrodes is very simple and introduce several superior specifications, like easy sample conditioned, quick restraint, highly eclectic, expanded usable and linear range of concentration, available portable tools with a very low limit of detection, completed in turbid, viscous, and/or colored solutions and economic.

Some of the heterodiazo dye ligands which have the ability to form strong and stabilized ion-associate complexes with some active cations were synthesized to detect them in pharmaceuticals, food products, and real environmental samples applying spectrophotometric methods[33- 34].

The cited ligand [BrPPSAA] [35]; figure 2 has good sensitivity and selectivity coefficient. Therefore, we did not hesitate to apply its usefulness applicability for the construction of chitosan membrane sensors.

In this research study, the designation and determination of newly chitosan membrane electrodes is described. The main component in a polyvinyl chloride ; (PVC) matrix eclectic electrode is the ion-associate complex of nano-chitosan with the ligand [BrPPSAA]. The electrode is effectively applied for the nano-chitosan determination in food supplements and fruit juice with nano chitosan.

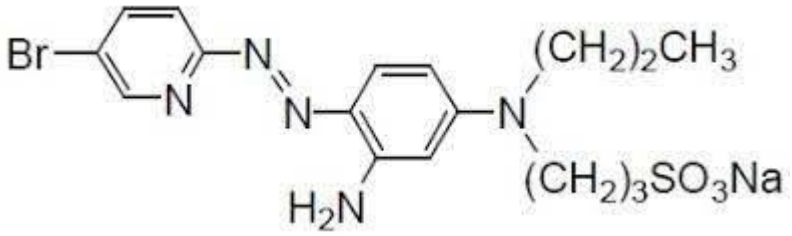

Figure 2. Chemical structure of the cited reagent [BrPPSAA]

2. EXPERIMENTAL

2.1, Food Supplements Samples, Chemicals and Materials

Chlorides of calcium, chromium, and/or zinc, L-Carnitine, promethazine, diclofenac potassium, citrimax and metronidazol. Polyvinyl chloride; PVC and TEHP; [tris-(2- ethylhexyl) phosphate] were Aldrich products. Hydrochloric,hydrofluoric,and sulfuric acids,tetrahydrofuran,and TBP(tributyl-phosphate) from Merck [Germany].

Food supplements containing nano-chitosan with abreviations were(Fat out,Chitocal, Chitoclear,Chitoseen-F,and Chitosan Plus) capsules were obtained from the Egyptian and Saudi Arabia local markets.The cited ligand [BrPPSAA] was conditioned and prepared as listed previously[35].

2.2. Stock Solutions Conditioned

All procedures were completed with analytical grade chemical reagents. Stock solutions of Ca^{2+}, Cr^{3+},and/or Zn^{2+} of 0.1 Mr solutions were weighed and dissolving the computed amounts of each one in bidistilled H_2O. Solutions of 10^{-7} - 10^{-2} M were conditioned by dilution. Low molecular weight of acid-soluble chitosan was provided from Sigma-Aldrich Company,(USA). Stock solution of nano-chitosan was conditioned by dissolving 100 mg in 100mL of 1% (v/v) aqueous acetic acid; it dissolves easily on trembling. Appropriate dilutions can be used when needed,and the solution should be stayed between 0 and 4°C.

2.3. Sample Preparation and Nano-Chitosan Assay in Food Nutritional Supplements

Food nutritional supplements; (Fat out, Chitocal, Chitoclear, Chitoseen - F and Chitosan Plus) capsules were selected for analysis. In all cases, the well-blended grounded content of 15 capsules was utilized in the evaluation. A weight of 100 mg of the powder was converted into volumetric flask and dissolved in 50 mL aqueous acetic acid solution (1%, v/v) then completed to mark. Various aliquots (20,30,40,50,60,70,80,90 and 100 μL) of this solution were assessed employing the suggested method as described before.

For the preparation of fruit juice with Nano chitosan,the ripe orange and mango fruits carefully sorted, proper washed then extracted by pulper machine, the resultant pulp was homogenized, sieved with 25 mm sieve. The total soluble solids (T.S.S) of both juice were evaluated (8.5 for mango juice and 10.3 for orange juice). The pH of both juice were adjusted to 4.3 using 20% citric acid solution

then 5.8 mg of nanochitosan was added to 20 ml of each juice and vigorously mixed for 10 min then stored in refrigerator (4 ^{o}C) till evaluation of nano chitosan content using the prepared electrode (within 24 hr).

2.4. Fabrication of The Developed Electrode

The fabrication of the nominated membrane was designed as reborted previously[36]. It consists of a coloumn electrode of Teflon exchangable tube and a body completed with a liquid membrane phase + Ag/Ag Cl an electrode internal reference.

2.5. Optimization of the Potential Layer conditions

The sensitivity and selectivity of the membrane are effectively influenced by the nature and composition of utilized additives. Therefore, the influence of various membrane compositions on the specific restraints of the suggested electrode was examined to optimize the best composition of the designed sensor. Plasticizer is the important cmponent of the designed electrode and has a crucial influences on the mobility, the state of ionophore molecules and dielectric constant of membrane. It did not only affect the workability of the membranes, but also improve the usable concentration range, stability and duration-time of the suggested membrane sensor. Therefore, by detecting constant amount of PVC (0.44 g), by changing the ratio between the compound [CHN(BrPPSAA)] and the plasticizer TEHP as follow: [(0.03g, 0.53g) (0.04g, 0.52g), (0.05g, 0.51g), (0.01g, 0.55g), (0.02g, 0.54g), and(0.06g, 0.50g),respectively]. The mixture were blended to provide the layer of the proposed electrode. A Teflon tube with an electrode of Ag/AgCl was completed with the recently and freshly prepared blended, then transferred into a gel by heating at 375 K temperature for 25 mins. The electrode was soaked for two hrs. in 10^{-3} M nano-CHN solution fter cooling.

2.6. Measurements of the EMF of the developed Electrode

An Orion 90-00-01 solution containing 0.55M potassium chloridel,1.5 M potassium nitrate, ,0.05 M sodium chloride and 40 % formaldhyde 1 ml was employed to reach the stabilized bridge of the reference electrode. An Orion 90-02 reference electrode was applies with a mechanical stirrer to give a veracity of 0.1 mV at ambient temperature for gauging the EMF of nano-chitosan fabricated system.

3. RESULTS AND DISCUSSION

The interesting validation parameters of the nominated nano-CHN membrane were examined to detect its crucial in practical utilizations.The detection limit,the specific slope, time of response, selectivity study,and pH influence on the developed electrode potential were studied.

3.1. The Suggested Nano-Chitosan Electrode Calibration Curve.

It is well known that the composition of membrane, additives employed and the solvent mediator nature effectively affect the selectivity and sensitivity of the sensor [37-39]. The plasticizers not only reinforce the utility of the sensors, but also progress the linearity range concentration, duration-time and stability of the membrane[4o-41]. Among the different trials to optimize the best membrane compositions that contain 0.01g compound [nano-CHN(BrPPSAA)] with a mixture of,0.55 g TEHP,and 0.44 g PVC,It displays the best behavior of the membrane electrode. The calibration curve Fig.3 showed a good Nernstian response with a slope of 54.00 mV/decade for four replicate monitoring in the usable rectilinear range of 1.0×10^{-7}-1.0×10^{-2} M with a very low detection limit ($1.47x10^{-8}$) M as detected from the intersection of the two extrapolated segments of the calibration graph.

The interesting specific parameters of the designed and fabricated nano-CHN electrode are summarized in Table 1.

Table 1. Interesting validation parameters of the suggested nano-CHN electrode matrix (reference electrode Ag/AgCl).

Slope /mV/decade	54
Intercept/mV	- 49
Detection limit/mol dm^{-3}	$1.47x10^{-8}$
Measuring range/mol dm^{-3}	$1.0x10^{-7}$-$1.0x10^{-2}$
Time of response /s	10
Long life/d	150
pH Usable range	4.0-6.0

3.2. Interference Study

The selectivity study of the nano-CHN developed electrode related to intervention ions was examined by the separate solution or the MPM, (matched potential) method described earlier[42] using the following equations:

$\log K^{pot}_{ij} = E_j - E_i / S - (Z_i / Z_j - 1) \log a_i$, $K^{pot}_{CHN/M} = \frac{ai}{ai\frac{zi}{zj}}$

where ai is the CHN activity, Ei is the potential of CHN,Ej is the potential of the interfering ion,zi and zj are the charges of CHN and interfering ions, respectively,M refers to the interfering species, and S is the slope of the electrode calibration plot.

By utilizing the separate solution method, at the magnitude of EMF,the potential –160 mV,and 0.001 M CHN. For the MPM, the equation is:

$K^{pot}_{CHN/M} = \frac{ai}{ai\frac{zi}{zj}}$

The produced results are detailed (Table 2).

Table 2. The selectivity behavior of nano-CHN suggested sensor matrix(reference electrode Ag/AgCl).

Separate Solution Method(SSM)			Matched Potential Method
K	$E_i = E_j$	$a_i = a_j$	MPM
Ca^{2+}	0.251 + 0.0033	0.282 + 0.020	0.226 + 0.0120
Zn^{2+}	0.198+ 0.0023	0.196 + 0.012	0.195 + 0.0340
Cr^{3+}	0.181 + 0.0121	0.182 + 0.001	0.184 + 0.0031
Phosphate	0.093 + 0.0022	0.098 + 0.011	0.094 + 0.0021
Metronidazol	0.086 + 0.0012	0.084 + 0.012	0.081 + 0.0014
Citrimax	0.075 + 0.0012	0.077 + 0.011	0.076 + 0.0021
L- Carnitine	0.064 + 0.0021	0.062 + 0.015	0.063 + 0.0013
Promethazine	0.053 + 0.0034	0.051 + 0.018	0.052 + 0.0031
Diclofenac potassium	0.041 + 0.0021	0.043 + 0.006	0.042 + 0.0022

3.3. Dynamic Time of Response of the developed Nano-CHN Sensor

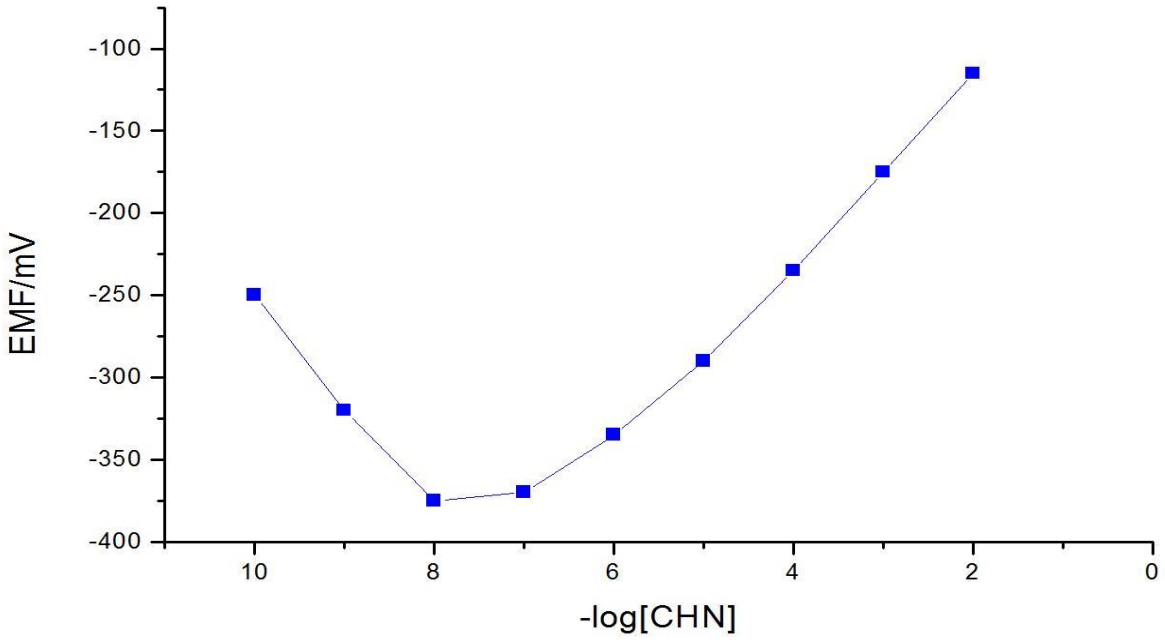

Figure 3. The proposed CHN electrode calibration curve in the linear concentration range 10^{-7}-10^{-2}M.

The response time of the designed membrane sensor is of great crucial in practical analytical applications. After injecting the concentrated standard solution,diluted by adding water (1:1).The employed solutions for the restraint time estimation of the understudied sensor have these specifications: c1:c2=1:100, v1:v2=1: 20, where c1 is the concentration of the sample,c2 the standard

concentration,v1 is the sample volume and v2 is the volume of standard. The results obtained are introduced in Fig.4.

The restraint of the electrode is reproducible after 10 seconds of adding chitosan which is agree with the previously published worhs[43-44[. At the injection moment of the concentrated specimen the timer is began,the fast and stabilized recording of potential indicating the time taken for completing the titration. As depicted in Fig. 4,the suggested sensor attains its equilibrium response in a very short time(10s) over the whole concentration range.

3.4. Effect of pH on The Sensor Potential

The pH behavior on the designed membrane potential was examined by monitoring the potential based on the chemical properties of nano-chitosan. Adding few drops of sodium hydroxide or hydrochloric acid to the sample of 0.001 M nano-chitosan cations understudying. The pH was registered after each addition of the acid or base, the electromotive force; EMF of the CHN electrode system/reference was read after the sensor's response stabilized. The pH effect on the EMF is depicted in Fig.5. Below and above this pH range(4.0-6.0)the sharp decrease in potentials may be arised from the incomp-leteness of the complexation reaction or the hydrolysis of CHN cations[45-46].At higher pH values,the potential decreases(-159 at pH 7.0,-167 at pH 8.0,-174 at pH 9.0,and -184 at pH10) due to the hydrolysis of nano-chitosan cations or the incompleteness of the complexation reaction. At lower pH values the potential increases (-138 at pH 3.0,-131 at pH 2.5,and -125 at pH 2.0) which is due to the electrode restraints to hydronium ions and nano-chitosan cations.

3.5. The Lifetime of the suggested Nano-CHN Electrode

The duration-time of the nano-CHN suggested electrode was examined by calculating the slopes of the characteristic designed membrane stored at 4 ^{o}C [47-48]. The lifetime of the electrode is about five months according to the basis of the obtained data. In freshly prepared solutions systematic regular studies were carried out once a week in a regular manner for at least seven months. Reproducible monitoring was obtained through five months. It was indicated that a little decrease in the slope of the developed sensor by 1.0 mV /decade from 54.00-53.00 mV/decade and an increase in the detection limit. Afterward, the slope of the sensor reduced strongly,whilst the detection limit is increased to be(from 44.65 to 38.26 mV/decade and 2.4×10^{-7}to1.3×10^{-6} M, respectively) were noticed as indicated previously[47-48]. This possibly produces from the nomination of the membrane components. Therefore,the lifetime of the developed sensor is about 5 months, related to the basis of the produced data.

3.6. Determination of Nano-CHN in Food Nutritional Supplements and Juice

The determination of nano-CHN cations in food nutritional supplements was investigated employing the prepared sensor to examine its validation usefulness utilities. The methods of standard additions

and calibration curve were employed. The amounts of nano-CHN in the samples were computed from predetermined calibration plots and their statistical validation analysis are in detail(Table 3).

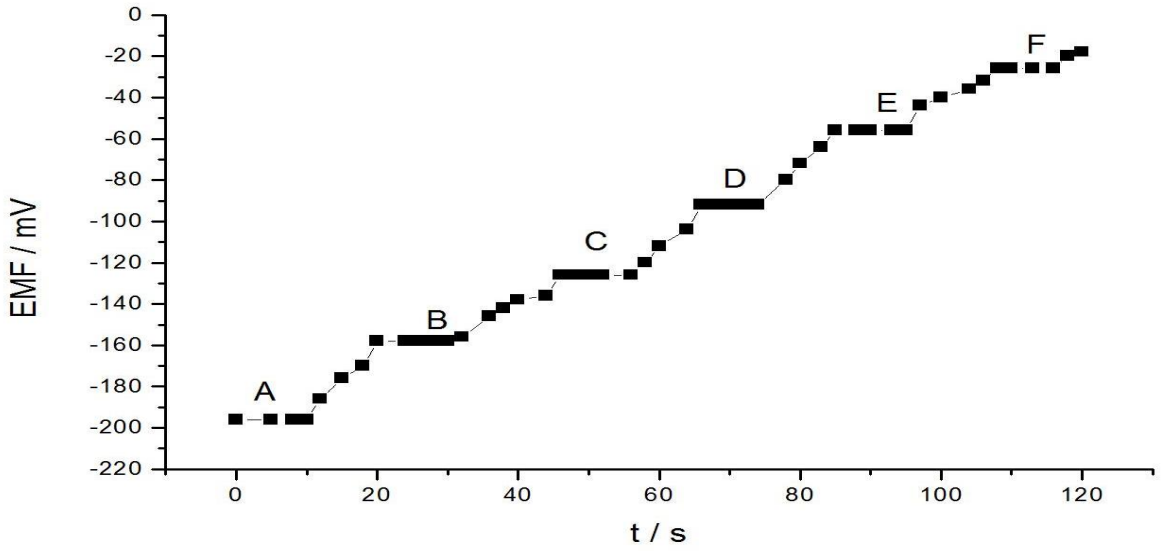

Figure 4. Response time of nano-CHN sensor cations concentration,(A)10^{-7}M,(B)10^{-6} M,(C)10^{-5} M,(D)10^{-4} M,(E)10^{-3}M and (F)10^{-2} M.

Determination of chitosan in food nutritional supplements were examined to assess the execution of the suggested method for real samples. The data are depicted in Table 3 proved that the existing contents of chitosan capsules is 500 mg/capsule. In addition, the calibration curve method is preferred in the determination of nano-chitosan (Recovery from 95.45-99.14 %) while the standard additions method is less recommended (Recovery from 89.66-96.55 %) prove that the suggested process is appropriate for the nano-chitosan estimation in trace amounts of foodstuff and prepared juice specimens other than the different sensors described before for chitosan determination[15-19].

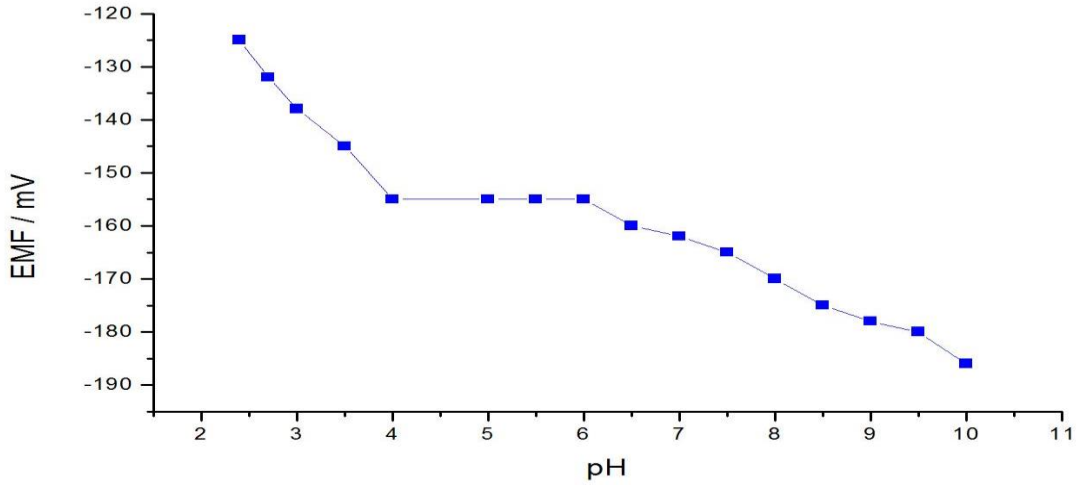

Figure 5. Dependence of the suggested electrode response on the pH in nano-CHN cations concentration [10^{-7} - 10^{-2} M].

Table 3. Nano-Chitosan (CHN) content in some food supplements and prepared juice as determined by matrix (reference electrode Ag/AgCl) membrane

Samples 500 mg Chitosan content / Capsule	Sample taken (µ L)	CHN Calculated mg	Calibration Curve Method			Standard addition Method		
			CHN found mg	Recovery %	Relative Error %	CHN Found mg / Kg	Recovery %	Relative Error %
Fat Out	20	0.029	0.028	96.55	0. 1	0.026	89.66	0.3
	30	0.044	0.043	97.73	0.1	0.041	93.18	0.3
	70	0.102	0.100	98.04	0.2	0.098	96.08	0.4
Chitocal	40	0.058	0.056	96.55	0.2	0.052	89.66	0.6
	60	0.088	0.086	97.72	0.2	0.083	94.32	0.5
	80	0.116	0.115	99.14	0.1	0.112	96.55	0.4
Chitoclear	30	0.044	0.042	95.45	0.2	0.040	90.91	0.4
	60	0.088	0.085	96.59	0. 3	0.082	93.18	0. 6
	90	0.131	0.129	98.47	0.2	0.126	96.18	0.3
Chitoseen-F	30	0.044	0.042	95.45	0.2	0.040	90.91	0.4
	50	0.073	0.071	97.26	0.2	0.069	94.52	0.4
	80	0.116	0.113	97.41	0. 3	0.109	93.96	0.7
Chitosan Plus	30	0.044	0.043	97.72	0.1	0.041	93.18	0.3
	60	0.088	0.087	98.86	0.1	0.084	95.45	0.4
	100	0.145	0.140	96.55	0. 5	0.139	95.86	0.6
Orange Juice	20 mL	5.80 mg	5.78 mg	99.66	0.02	5.73 mg	98,79	0.07
Mango Juice	40 mL	11.60 mg	11.57 mg	99.74	0.03	11.52 mg	99.31	0.08

- The averages of (six) estimations.

3.7. Comparison with the Previously Published Sensors

The provided results by the designed chitosan sensor were statistically treated and compared with the recently various published sensors. Table 4 displayed a comparison among some of the interesting validation measuring factors of the quantitative determination of nano-CHN cations applying recently various sensors listed before. The detailed comparison (Table 4)indicated that the suggested electrode provides reliable and acceptable results for nano-CHN cations food product specimens. As can be seen from Table 4 that the nominated electrode exhibits a usable linearity range(1.0×10^{-7}- 1.0×10^{-2} M) that is better than the recently reported CHN sensors[15-19]. It is specified by a long duration-time,(150 days) in comparison with the other previously published snsors, the lowest detection limit (1.47×10^{-8} M)is that provided by the suggested electrode. Further, the proposed electrode has several properties in comparison with the other recently published, such as: easy to design, economically. Thus, it can be effectively applied in all analyses with other mentioned sensors for the detection of chitosan cations.

Table 4. Interisting validation parameters of nano-CHN [BrPPSAA] in comparison with other reported electrodes for chitosan determination in acedic medium.

Ref.	Usable linearity range (M)	Limit of detection (M)	Real Samples
Proposed electrode data	1.0×10^{-7}-1.0×10^{-2}	1.47×10^{-8}	Food supplements and Juice
15	5.0×10^{-6}-1.5×10^{-3}	0.17×10^{-6}	Tap water
	5.0×10^{-6}-0.9×10^{-3}	0.89×10^{-6}	
16	2.0×10^{-5}-1.0×10^{-2}	3.60×10^{-6}	Industrial waste water
17	9.5×10^{-5}-1.4×10^{-4}	2.90×10^{-7}	Pharmaceutical formulations, synthetic urine and river water
18	4.97×10^{-6}-3.01×10^{-5}	2.09×10^{-6}	Natural raw waters samples
19	1.0×10^{-6}-1.5×10^{-4}	0.01×10^{-5}	Serum, plasma and urine samples

No intervention was noticed from the ingredients present in the samples understudying. The calibration curve depicted a super linearity response on an expanded usable range of concentration. Most of the methods display excellent recovery closed to the known values and there is no considerable drift for either veracity or exactness were presented.

4. CONCLUSION

In this study, a suggested nano-chitosan;(CHN) sensor was developed. The designed sensor is specified by super validation characteristics: the Nernstian specific slope,very short time of response and long duration-time.The interesting validation parameters of the suggested sensor are displayed (Tables1and 2).

The designed sensor was employed for nano-chitosan cations determination in food supplements and prepared juice that is used in common. The calibration curve method and that of standard additions were employed. The data analysis indicated that the calibration curve method is the best in the detection of nano-chitosan(Recovery from 95.45-99.14 %) whilst the method of standard additions is less recommended (Recovery from 89.66- 96.55 %). Thus,the mistake is not exceeding 1% owing to the repeatability of the technique.The method of sensor designation was set up as preciseness and exactness as compared to the recently published methods that are commonly employed in their estimation in food products and prepared juice(Table 4).

In general,the particularity of the produced data was excellent which is due to the importance of the eclectic samples employing the designed membrane.The time required in the applications is examined with no influence on the veracity, reproducibility, and preciseness of the producing data.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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