

Determination of Nitrite in Environmental Samples Using Chemically Modified Carbon Paste Electrode Based on New Co(III)-benzopyran-4-one Schiff Base Complex

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Abstract: Nitrite chemically modified carbon paste electrode based on Co(III)-benzopyran-4-one Schiff base complex is described. The electrode revealed a Nernstian response over a wide nitrite ion concentration range (9.1×10^{-6} – 1.5×10^{-2} mol·L⁻¹). The detection limit of the sensor is 7.0×10^{-6} mol·L⁻¹. The best performance was obtained with a paste composition of 4 % Co(III)-benzopyran-4-one Schiff base, 2 % cetylpyridinium chloride (CPC), 42 % graphite, and 52 % dibutyl-butyl phosphonate (DBBP). The potentiometric response of the sensor is independent of the pH of solution in the pH range of 3.0–8.5. The electrode exhibits a very fast response time reaching to 20 s and good selectivity over a variety of common inorganic anions, including Cl⁻, Br⁻, NO₃⁻, F⁻, SO₄²⁻, CO₃²⁻, S²⁻, HPO₄²⁻, S₂O₃²⁻, and CH₃COO⁻. The selectivity behavior of the proposed sensor shows substantial improvements in comparison to many previously reported electrodes for nitrite ion. The electrode was successfully applied also to the monitoring of nitrite ion in drinking water, soil and for determination of nitrogen dioxide in the air.

Keywords: Nitrite; Carbon paste electrode; Co(III)-benzopyran-4-one Schiff base; Potentiometry.

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Introduction

Nitrite ion is of great significance because it is one of the parameters of nitrogen fixation, denitrification, sedimentation, and many other anthropogenic processes that have an impact on

the quality of natural, surface, and underground water [1]. There has been increasing interest in the trace determination of nitrite due to its important role in environment processes, its toxicity, and suspected carcinogenicity in the human body. Among various nitrite sensors, electrochemical ones have attracted much attention because of quick response, high sensitivity, as well as, abilities to be miniaturized. Several nitrite ion-selective electrodes based on Vitamin B12 [2], butylphthalocyaninecobalt [3], tetraphenyl-porphyrinato) Co(III) [4], rhodium(III) 5,10,15,20-tetra(*p*-tertbutyl-phenyl)porphyrin chloride [5], uranyl salophen [6], Co(II)-salophen [7], cobalt(II)-salen [8], and octakis(benzylthio)-tetraaza-porphyrin Co(III) [9] have been reported in literature.

The potentiometric selective determination of many anions is difficult because the classical membrane electrodes for anions based on various anion exchangers exhibit similar selectivity sequence (lipophylic organic anions > ClO_4^- > IO_4^- > SCN^- > Γ^- > NO_3^- > Br^- > Cl^- > HCO_3^- > $\text{F}^- \geq \text{H}_2\text{PO}_4^-$) [10]. This is the reason why highly hydrated anions such as nitrite, chloride, and fluoride are difficult to monitor due to significant interference from more lipophilic anions that may be presented in the sample. So, in the field of anion selective electrodes, the need for ionophores with improved selectivity and sensitivity is increased.

The use of metalloporphyrins as ionophores in polymeric membrane electrodes showed an excellent anion selectivity pattern that differs significantly from the classical Hofmeister pattern. The ability of the porphyrins to have a Lewis acidic metal as the coordinating site, together with the fact that the binding affinity of this central metal could be controlled, to a large degree, by the surrounding porphyrin ring as well as the fifth or sixth ligand attached to the metal, makes them interesting anion carriers. Electrode selectivity towards anions in these cases is not governed by anion lipophilicity as in the case of dissociated ion-exchanger, but by specific chemical interactions between the metalloporphyrin from the membrane and the anions in the sample solution [11–15]. The enhanced selectivity is highly dependent on the type of the metal–ion center of the ionophore that leads to a selective ligation with a particular anion, or the existence of selective complementary interaction between the target anion and the carrier.

Schiff base complexes are interesting class of ionophores that exhibited non–Hofmeister selectivity pattern when doped in polymeric membranes [16–18]. Schiff base is known to form stable complexes with transition metal ions, and it acts as an ion carrier in the polymeric membrane electrode. The characteristic of Schiff base gives geometric configuration, cavity control of host-guest complexation, modulation of its lipophilicity, and provides remarkable selectivity, sensitivity and stability for a specific metal ion. The resulting

Schiff base complexes have attracted increasing attention in the area of ionic binding and selectivity due to their unique properties and reactivity.

In this work, a new sensitive, selective chemically modified carbon paste (CMCP) electrode for nitrite was developed based on Co-Schiff base complex. This Schiff base (Fig. 1) was derived from condensation of 6-formyl-5,7-dihydroxy-2-methylbenzo-pyran-4-one with trimethylenediamine.

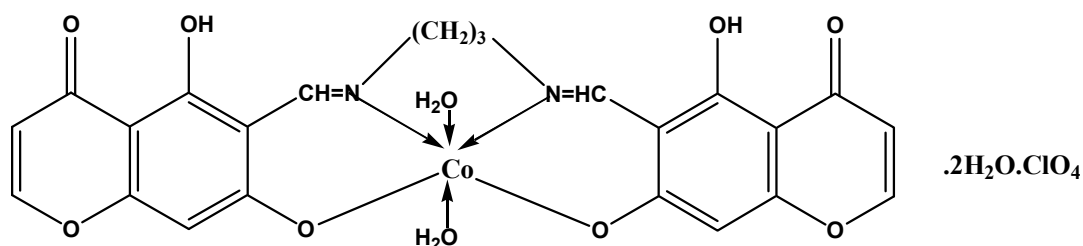


Fig. 1: Structure of Co(III)-benzopyran-4-one Schiff base complex.

Experimental

Apparatus and Reagents

For potential measurements a *JENWAY* 3010 digital pH/mV meter was used. A *SENTEK* R1/2MM Ag/AgCl electrode was used as the outer reference electrode. *Millipore Elix S* (Automatic Sanitization Module, ASM) was used for obtaining the deionized water. *CARY 50* Probe UV-Visible spectrophotometer (*Varian*) was used for the spectrophotometric measurements, and *Dionex* ISC-1000 was used for ion-chromatographic determination of nitrite ion.

Graphite powder, AgNO_3 , Co(II) perchlorate, cetylpyridinium chloride (CPC), sodium tetratphenylborate (NaTPB), cetyltrimethylammonium bromide (CTAB), 1,3-trimethylenediamine, and *o*-nitro-phenyloctyl ether (*o*-NPOE), dibutyl phthalate (DBP), dibutyl-butyl phosphonate (DBBP), tricresyl phosphate (TCP), and dioctyl sebacate (DOS) were purchased from *Aldrich*.

Solutions

Stock solution of $0.1 \text{ mol} \cdot \text{L}^{-1}$ sodium nitrite (El-Nasr Chemicals product) was prepared by dissolving 0.69 g NaNO_2 in 100 ml deionized water, standardized spectrophotometrically [19] and the solution was kept in the dark bottle in the refrigerator. To investigate the selectivity of the proposed electrodes,

0.1–0.5 mol·L⁻¹ salt solution of each of the following ions Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, S²⁻, F⁻, SO₃²⁻, HPO₄²⁻ and SCN⁻ were prepared.

Preparation of *N,N'*-bis[(5,7-dihydroxy-2-methyl-4-oxo[b]benzopyran-6-yl)methylene] trimethylenediamine] Schiff Base (Benzopyran-4-one Schiff Base). Benzopyran-4-one Schiff base was prepared by the drop wise addition of trimethylenediamine (0.005 Mol) in 20 ml ethanol with continuous stirring to a solution of 6-formyl-5,7,dihydroxy-2-methylbenzopyran-4-one (0.01 Mol). The mixture was stirred at room temperature for at least 30 min and the solid obtained was filtered off, washed with ethanol and recrystallized from DMF [20].

Preparation of the Co-benzopyran-4-one Schiff Base Complex. A hot ethanolic solution of the Co(II) perchlorate (10 mL) was gradually added to (20 mL) solution of benzopyran-4-one Schiff base derivative in 1:1 molar ratio and the solution was stirred on a water bath for 2 h during which the metal complex precipitated. If the complex did not precipitate, ammonia solution was added drop wisely to adjust the pH value in the range 6–7. The resulting precipitate was filtered off, washed with water, ethanol then diethyl ether, and finally air-dried [21].

Preparation of Carbon Paste Electrodes

The electrodes were prepared as described [22]. The modified paste was prepared by mixing the appropriate weight of ionophore and high purity graphite with acetone. The mixture was homogenized, left at room temperature to evaporate acetone, then a weighed amount of plasticizer was added and the mixture was very intimately homogenized by careful mixing with an agate pestle in agate mortar. The paste was then packed into the hole of the electrode body. The carbon paste was smoothed onto a paper until it had a shiny appearance and used directly for potentiometric measurements without preconditioning.

Selectivity of the Sensor

Potentiometric anion selectivity coefficients were determined by the matched potential method [23, 24]. In this method, selectivity coefficient $K_{\text{nitrite},J}^{\text{MPM}}$ is given by:

$$K_{\text{nitrite},J}^{\text{MPM}} = \frac{\Delta a_{\text{nitrite}}}{a_B} = \frac{a'_{\text{nitrite}} - a_{\text{nitrite}}}{a_B} \quad (1)$$

where $\Delta a_{\text{nitrite}}$ is determined by measuring the change in potential upon increasing the concentration by a definite amount of the primary ion activity from an initial value of a_{nitrite} to a'_{nitrite} and a_B represents the activity of the interfering ion added to the same reference solution of activity a_{nitrite} which brings

about the same change in potential. The activity of nitrite as the reference solution was taken as $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ in this study.

Potentiometric Determination

The standard addition method was applied [25]. In this method, the proposed electrode was immersed into a sample solution of 25 mL with unknown concentration ($\sim 10^{-7}$ – $10^{-4} \text{ mol} \cdot \text{L}^{-1}$) sample and the equilibrium potential of E_u was recorded, then 0.1 mL of $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ of standard nitrite solution was added into the test solution and the equilibrium potential (E_s) was obtained. From the potential change $\Delta E = (E_u - E_s)$ one can determine the concentration of the test sample using the equation:

$$C_x = C_s \left(\frac{V_s}{V_x + V_s} \right) \left(10^{n(\Delta E/S)} - \frac{V_x}{V_s + V_x} \right)^{-1} \quad (2)$$

where C_x is the concentration to be determined, V_x is the volume of the original sample solution, V_s and C_s are the volume and concentration of the standard solution added to the sample to be analyzed, respectively, ΔE is the change in potential after addition of certain volume of standard solution, and S is the slope of the calibration graph.

Preparation of Samples Used for Analysis

Air Samples. Different samples are collected from Shoubra location (Cairo). Air is drawn through an air intake (inverted funnel) and a glass filter impregnated with sodium iodide and sodium hydroxide. Nitrogen dioxide is adsorbed in this filter and the iodide reduces NO_2 to nitrite. The hydroxide is converted to carbonate during sampling due to uptake of carbon dioxide. The nitrite formed on the glass filter is collected with deionized water. After extraction, the nitrite concentration is determined potentiometrically using the proposed nitrite-CMCPE and the results were compared to the reference spectrophotometric method (Griess method). The method involves conversion of nitrite to nitrous acid in acidic medium followed by diazotization of sulphanilamide or sulphanilic acid and formation of diazonium salt. The diazonium salt was then coupled to either N-(1-naphthyl)ethylenediamine or 1-naphthylamine to form azodye measurable at 540 nm [19].

Soil Samples. Samples were collected from different sites in Egypt, namely Cairo University, Sixth October, and New Cairo District. The samples weighing 5 g were dissolved in 100 mL deionized water and then filtered.

Water Samples. Water samples are collected from tap water in Cairo University Laboratories and river water from El-Warrak location (15 Km north of Cairo, at 60 cm subsurface).

Results and Discussion

Some Schiff-base complexes of Co^{2+} have been previously evaluated as anion carriers [16–18], they showed that the electrically neutral Co^{2+} -salen is oxidized during the conditioning process to form a positively charged Co^{3+} -salen that accounts for the charged carrier operative response mechanism obtained for nitrite/thiocyanate. The diamagnetic nature of cobalt-benzopyran-4-one Schiff base complex (prepared from Co^{2+} -perchlorate) was taken as a good evidence for oxidation of Co^{2+} to Co^{3+} [21]. It has been reported that Co^{2+} complexes are readily oxidized to give Co^{3+} -complexes as the ultimate product during the conditioning period [26, 27]. Furthermore, ligands with empty π^* -orbitals, such as nitrite, greatly enhance the oxidation of metal-ions with filled d_{π} orbital (t_{2g}^6) via the back donation mechanism [27].

It has been shown that the nature and the oxidation state of the metal ion present in the complex influence the carrier mechanism exhibited by membranes doped with this metal-complex. With Co^{3+} -Schiff base, either neutral or charged carrier mechanism is possible [14]. The overall charge on Co^{3+} -complex is +1, and thus the cobalt metal center, which generally has a coordination number of 6, is capable of binding two axial ligands. Schematic structures of the Co^{3+} -Schiff base complex and the possible equilibria involving anions and neutral ligands are depicted in Fig. 2. From these equilibria, it is readily apparent that a charged carrier mechanism (A in Fig. 2) is only possible when the Co^{3+} -complex salt doped within the paste can dissociate significantly.

Composition of Nitrite Electrode

Co^{3+} -complex of 6-formyl-5,7-dihydroxy-2-methylbenzo-pyran-4-one Schiff base as an ionophore was found to be highly sensitive to nitrite with respect to several other anions. This complex is insoluble in many organic solvents, particularly tetrahydrofuran. Therefore, polymeric membrane electrode is difficult to prepare with this complex. The performance of carbon paste containing this complex as the sensor for nitrite was studied in this work in details. It is well known that the selectivity, linear range, and sensitivity obtained for a given CMCPE depends significantly on the paste composition [28], the nature of the solvent mediator [29, 30], and any additive used [31]. Different amounts of Co(III)-Schiff base complex were used in different pastes and the potential response of the electrode in the

concentration range 1.0×10^{-6} – 1.0×10^{-1} mol·L⁻¹ nitrite solution was illustrated and the results are tabulated in Table I. As can be seen from data in Table I and calibration graphs depicted in Fig. 3, the increase in the amount of the complex increases the sensitivity of the electrode towards nitrite and the slope increased from -50.3 mV for 2.0 % complex to -54.8 mV for 4.0 % complex but the linear determination range decreased and the response time for both compositions was very long (4 min.).

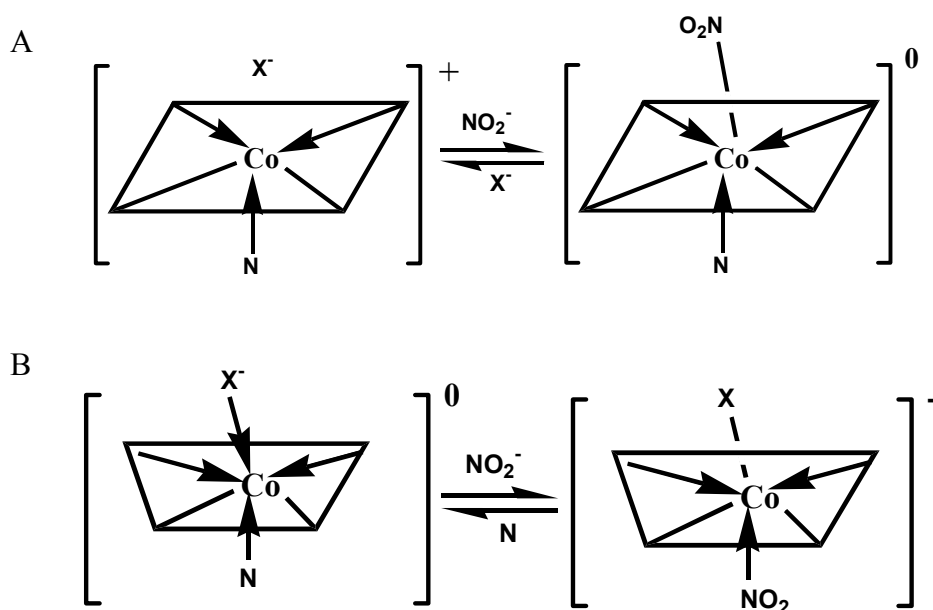


Fig. 2: Schematic representation of equilibria involved in possible charged carrier (a) and neutral carrier (b) mechanisms for Co³⁺-benzopyran-4-one Schiff base doped in graphite paste. N – a neutral axial ligand, and X⁻ – an anionic axial ligand.

The literature indicates that ion-selective electrode without an ionic additive should be avoided, since otherwise inherent ionic impurities could have a decisive influence on the electrode response characteristics [32]. The presence of lipophilic cationic sites in anion selective electrode is proving to have a beneficial effect on various sensor parameters. In general, the ohmic resistance and detection limit are lower, with less interference from anions at high sample activities. The selectivity and response behavior are improved and, in cases where the ionophore has poor extraction capabilities, the sensitivity of the sensor is enhanced. In addition, this additive may catalyze phase-transfer processes in cases when the kinetics at the sample/paste interface is limited [8].

Table I: Compositions and slope for calibration curves for nitrite-chemically modified carbon paste electrodes.

No.	Composition (%)				Slope (mV)	Detection limit (M)	Linear range (pNO ₂ ⁻)	Response time (s)
	Ionophore	Graphite	DBBP ^a	CPC ^b				
1	3	43	55	–	–51.8	1.99×10 ⁻⁵	4.90–2.10	240
2	4	43	54	–	–56.9	1.32×10 ⁻⁵	4.70–2.10	210
3	5	42	54	–	–53.0	1.02×10 ⁻⁵	5.04–2.10	240
4	4	42	53	1	–51.6	5.01×10 ⁻⁵	4.07–1.80	60
5	4	42	52	2	–60.3	7.00×10 ⁻⁶	5.04–1.82	20
6	4	42	51	3	–52.3	2.29×10 ⁻⁵	4.39–2.07	20

^a dibutylbutyl phosphonate.

^b cetylpyridinium chloride.

Therefore, the effect of the additives on the response of the nitrite electrode using sodium tetrphenylborate (NaTPB) as an anionic additive and cetyltrimethylammonium bromide (CTAB) or cetylpyridinium chloride (CPC) as cationic additives was studied.

Addition of NaTPB to the paste produces an electrode with extremely non satisfactory characteristics. The presence of CTAB as cationic additive results in an electrode with a narrow linear range and relatively high detection limit. The use of CPC as a cationic additive improves the sensitivity and the response characteristics of the present electrode. The influence of the amount of this additive on the characteristics of nitrite sensor was investigated by using different paste composition. Table I shows that the electrodes based on 2–4 % ionophore and without any additives (electrodes Nos. 1–3) exhibit near Nernstian response of the calibration graph, but with a very long response time of about 4 min.

Addition of 1–3 % of CPC to the paste containing 4 % Co³⁺-complex (Nos. 4 and 6) improves the linearity range of the electrode in addition to a drastic decrease in the response time which reaches to about 20 seconds with slope of –60.3 mV for the paste containing 2 % CPC. It was found that the electrode based on the paste containing 4 % ionophore, 2 % CPC, 42 % graphite, and 52 % DBBP exhibits the best response characteristics with a lower detection limit of 7.0×10⁻⁶ mol·L⁻¹. Therefore, this composition was used to study various performance characteristics and applications of this electrode.

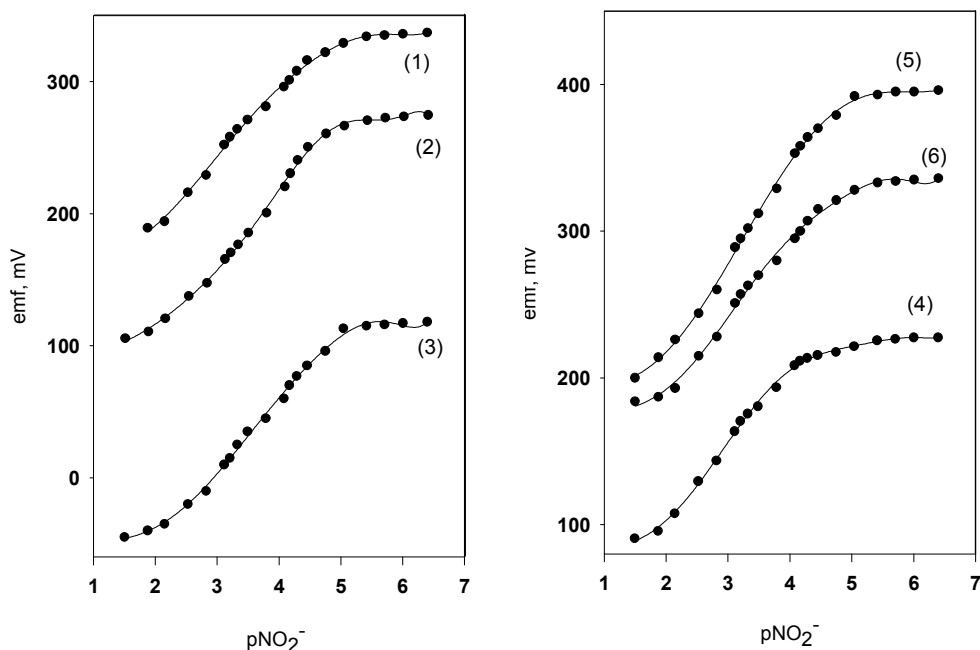


Fig. 3: Effect of paste composition on the characteristics of the calibration curves for nitrite-chemically modified carbon paste electrodes. (1) 3 % ionophore + 42 % graphite + 55 % DBBP, (2) 4 % ionophore + 42 % graphite + 54 % DBBP, (3) 5 % ionophore + 41 % graphite + 54 % DBBP, (4) 4 % ionophore + 42 % graphite + 53 % DBBP + 1 % CPC, (5) 4 % ionophore + 42 % graphite + 52 % DBBP + 2 % CPC, and (6) 4 % ionophore + 42 % graphite + 51 % DBBP + 3 % CPC.

Effect of Plasticizer

Since the nature of plasticizer influences the dielectric constant of the paste phase, the mobility of the ionophore and state of ligand [33], it was expected to play a key role in determining the ion-selective characteristics. It enhances the homogeneity of the paste and provides liquid channels within the paste which facilitates the movement of charge carriers thus, ultimately improves the response time and the sensitivity of the membranes. Various plasticizers (DBBP, DOS, DBP, NPOE, TCP, and corn oil) were added in varying amounts to the paste and the ion-selective characteristics of each composition were recorded.

The best electrode response towards nitrite (slope, working concentration range, and detection limit) was obtained with the use of 52 % DBBP as the solvent mediator. As can be observed from Fig. 4, that electrodes prepared with DOS, and NPOE gave a weak response towards nitrite with slopes of -24.8 mV, and -22.9 mV/concentration decade respectively.

While, TCP, DBP, and corn oil as plasticizers didn't give an appreciable response towards nitrite. Electrode plasticized with DBBP exhibits a linear response in the concentration range 9.1×10^{-6} – 1.5×10^{-2} mol·L⁻¹ nitrite solution with a slope of -60.3 mV and detection limit of 7.0×10^{-6} mol·L⁻¹. This is due to the best homogeneity provided by DBBP and its compatibility to the paste ingredients which results in a wide working concentration range and ideal Nernstian slope.

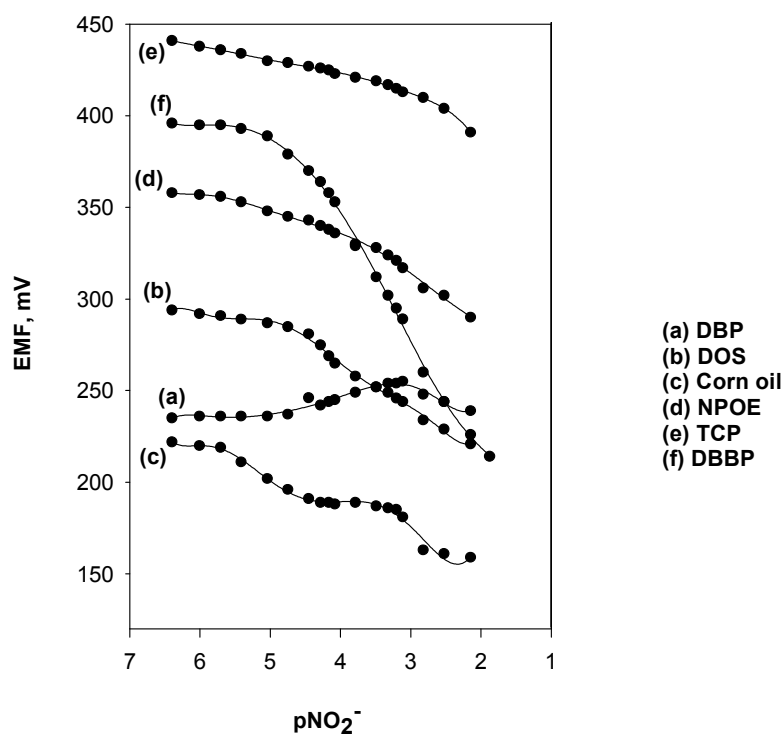


Fig. 4: Effect of different plasticizers on the response of nitrite-chemically modified carbon paste electrode.

Effect of pH

Nitrite sensitive electrodes based on Co³⁺-Schiff base complexes exhibited pH sensitivity, which was attributed to the affinity of the cobalt metal ion center for hydroxide ion [2,34]. The effect of pH of the test solution on the response of the nitrite-CMCPE was examined with a series of sample solutions (1.0×10^{-5} – 1.0×10^{-3} mol·L⁻¹). The pH was adjusted by adding small volumes of (0.1–1.0 ml) HCl or NaOH and the variation of potential followed. The potential–pH plots for the sensor are depicted in Fig. 5. It is obvious from the figure that the

potential response of the electrode is pH independent in the pH range 3.0–8.5 in 1.0×10^{-3} and $1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ NaNO_2 solutions and in the pH range 4.7–8.5 in $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ NaNO_2 .

The decreased potential of the electrode at $\text{pH} > 8.5$ can be explained in terms of the increased interference from OH^- ions, which may have a strong competing ligation reaction with NO_2^- ions for the central Co^{3+} ion. On the other hand, at $\text{pH} < 4.5$, the electrodes show an increased potential response, owing to the decreased concentration of free nitrite. This is because HNO_2 is a weak acid with a pK_a of 3.37, so that most of the NO_2^- ions will be converted to the unstable HNO_2 at lower pH of the test solution. This indicates that measurements of nitrite using the present CMCPE must be performed in a neutral or slightly acidic media to avoid the hydroxide interference at pH more than 8.0 or the loss of nitrite in the form of HNO_2 at pH values lower than 4.5.

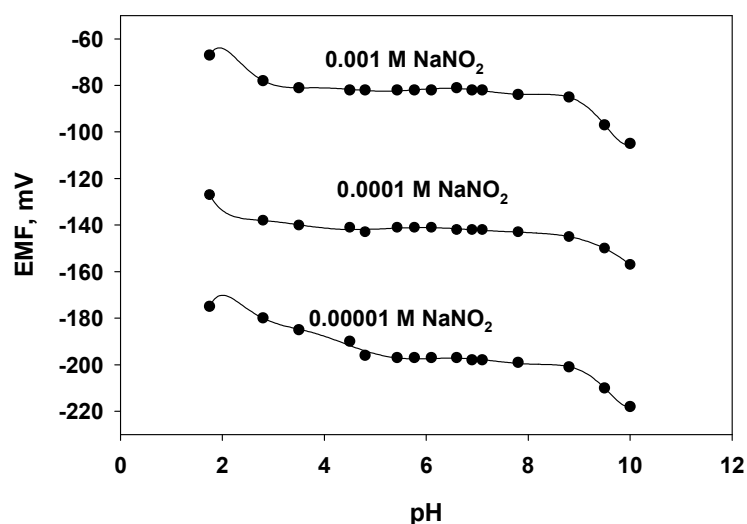


Fig. 5: Effect of pH of the test solutions on the response of the nitrite-chemically modified carbon paste electrode.

Response Time

The response time of the electrode which is the average time required for the electrodes to reach a stable potential response within $\pm 1 \text{ mV}$ of the final equilibrium value after successive immersion in a series of NO_2^- solutions, each having 10-fold difference in concentration was investigated. The resulting potential–time curve for the nitrite-CMCPE based on Co^{3+} -benzopyran-4-one Schiff base sensor obtained upon changing the concentration of nitrite from 1.0×10^{-5} to $1.0 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ is depicted in Fig. 6. As can be seen, the time needed to

reach the equilibrium value for the sensor is 20 s in concentrations of nitrite 1.0×10^{-5} and $1.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, and less than 20 s in concentrations of 1.0×10^{-3} and $1.0 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$. This is most probably due to the fast exchange kinetics of the complexation–decomplexation of nitrite ions with the complex at the test solution–paste interface.

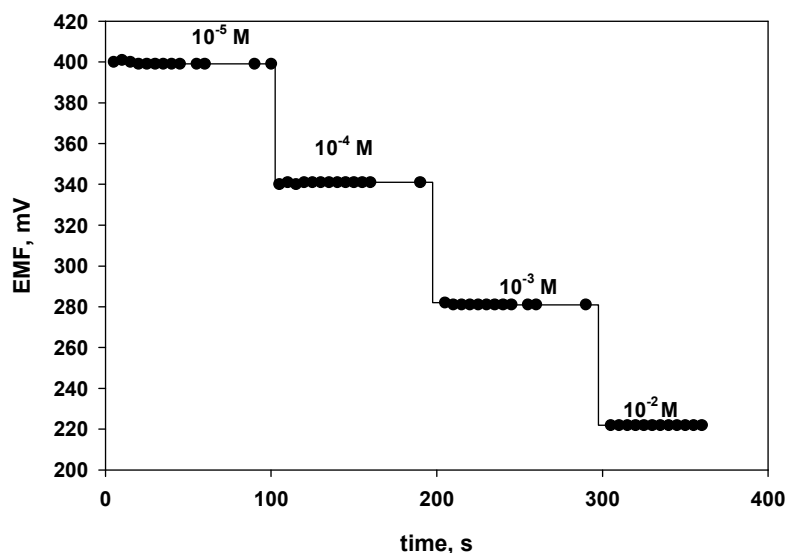


Fig. 6: Potential-time plot for the response of nitrite-chemically modified carbon paste electrode.

Homogeneity, Surface Renewal and Reproducibility of the Electrode

The main attraction of using the modified electrode is that the electrode surface can be renewed after every use. The electrode can be renewed by squeezing a little carbon paste out of the tube and a fresh surface is smoothed on a piece of weighing paper whenever needed [35]. Accordingly, a paste of optimum composition and suitable weight ($\approx 2.0 \text{ g}$) can be used for several months without any deterioration or change in the response of the electrode.

To test the paste homogeneity, the proposed electrode was applied for nitrite measurement in a $5.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1} \text{ NO}_2^-$ solution. The measurement was repeated ten times and after each measurement the electrode surface was renewed as explained above. The relative standard deviation (RSD) of the measurements was found to be 0.53, which is a reasonable value indicating the good homogeneity of the paste. The slope of the calibration graph was found to decrease slightly by $10 \text{ mV}\cdot\text{decade}^{-1}$ after three times of use. This

decrease may be attributed to surface contamination and memory effect. Every use of the electrode results in coordination of nitrite ions to some of the functional groups on the surface. Repeated use of the electrode results in a drop of the measured potential as the number of coordination sites at the surface is limited. Precision in potential measurements of a certain solution requires removal of the coordinated sites. Therefore, the electrode surface should be polished to expose a fresh layer for use.

Selectivity of Nitrite Electrode

The potentiometric response of the nitrite-CMCPE based on Co^{3+} -benzopyran-4-one Schiff base towards some inorganic anions in the concentration range 1.0×10^{-1} – 1.0×10^{-6} $\text{mol} \cdot \text{L}^{-1}$ nitrite solution is illustrated in Fig. 7 (a and b). It is obvious that, except for nitrite and thiocyanate ions, the slope of the corresponding potential versus $\text{pM}^{\text{n-}}$ plots is much lower than the expected Nernstian slope. This is due to the selective behavior of the complex towards nitrite in comparison to other anions tested. Also, the rapid exchange kinetics of the anion between the aqueous and the paste phase may enhance the selectivity of the electrode towards nitrite. This indicates a preferred interaction between Co^{3+} metal-ion center of the ionophore and NO_2^- or SCN^- anions in comparison to interactions with other anions.

This finding is consistent with the previously reported membrane electrodes based on different Co^{3+} lipophilic complexes (e.g., cobalt(III) complexes of porphyrins, corrins, and phthalocyanines that exhibited enhanced potentiometric responses toward $\text{NO}_2^-/\text{SCN}^-$) [2,14,34,36]. In contrast, membrane electrodes based on Co^{2+} -Schiff base complexes (e.g., Co^{2+} -nanophen and -napophen) exhibited selective interactions with iodide in comparison to other anions including thiocyanate and nitrite [16,17]. Co-benzopyran-4-one Schiff base is structurally related to corrin and porphyrin complexes in many aspects such as the limited structural flexibility when in comparison to the previously reported Co^{2+} -Schiff base complexes [16,17], and the fact that cobalt center in Co-benzopyran-4-one Schiff base occupies the four basal sites of a distorted octahedral geometry [37,38]. This coplanar nature of the Co-benzopyran-4-one Schiff base could result in an increased conjugation in the complex with a concomitant increase in the π -electron density around the cobalt metal-ion center [39]. Such an electronic effect could weaken the interaction with iodide ion and increases the interaction with anions such as nitrite and thiocyanate that have π -acceptor capabilities through back-donation.

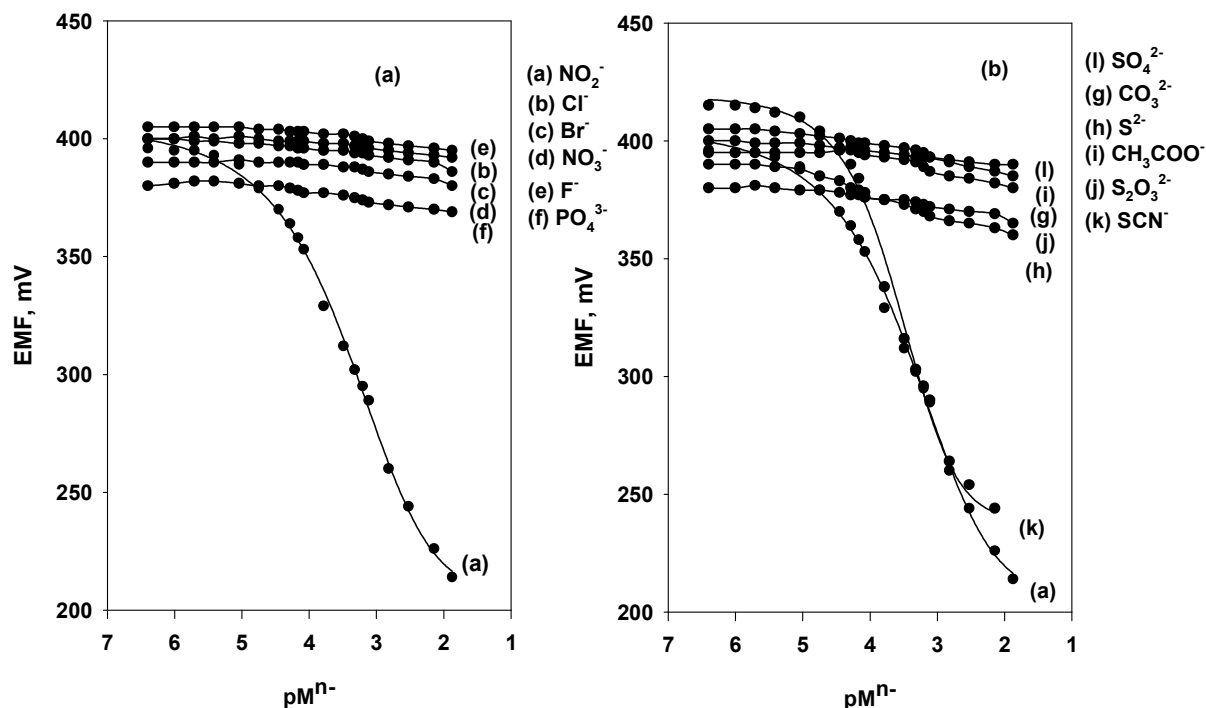


Fig. 7: Potentiometric responses of nitrite chemically modified carbon paste electrode, based on Co^{3+} -benzopyran-4-one Schiff base, towards various anions.

Potentiometric anion selectivity coefficients were determined by the matched potential method [23,24] and depicted in Table II. The $K_{\text{nitrite},J}^{\text{MPM}}$ values (Table II) are all in the order of 1.0×10^{-4} – $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ except for SCN^- . This indicates that except SCN^- all ions cause negligible interference on functioning of the proposed nitrite-CMCPE. It is interesting to note that this selectivity pattern significantly differs from the so-called Hofmeister selectivity sequence.

A comparison with the literature reported nitrite selective electrodes performance characteristics (slope, detection limit, linear range, response time, and interfering ions) was tabulated in Table III. As shown in the table, the sensor is of comparable performance with regard to interference and response time but has an excellent response towards nitrite with Nernstian slope of -60.3 mV which is better than other nitrite selective electrodes previously reported [3,6,36]. The investigated electrode has a lower detection limit of $9.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ than the previously reported electrodes [2,3,4,14] and wider linear range than most of previously proposed electrodes.

Table II: Selectivity coefficients for the nitrite-chemically modified carbon paste electrode.

Anion	$K_{\text{nitrite,anion}}^{\text{pot.}}$	Anion	$K_{\text{nitrite,anion}}^{\text{pot.}}$
Cl ⁻	2.13×10^{-3}	SO ₄ ²⁻	7.48×10^{-4}
Br ⁻	1.99×10^{-3}	CO ₃ ²⁻	3.49×10^{-3}
NO ₃ ⁻	4.67×10^{-3}	S ²⁻	9.54×10^{-3}
F ⁻	5.88×10^{-4}	HPO ₄ ²⁻	3.52×10^{-3}
SCN ⁻	1.65×10^{-1}	S ₂ O ₃ ²⁻	2.82×10^{-3}
CH ₃ COO ⁻	9.91×10^{-3}		

Analytical Applications

Nitrites are well known as toxic substances. The major effect of nitrites is the introduction of methaemoglobinemia as a result of nitrite reduction with hemoglobin. They can also react with some amines or amides present in the stomach forming N-nitroso compounds with carcinogenic action. These are the reasons why, nitrite content in water and food must be controlled and their determination must be currently done for checking the quality of the product.

In order to assess the applicability of the proposed nitrite sensitive electrode, the method was applied for the determination of nitrite content of different real samples such as drinking water and soil, in addition to the determination of nitrogen dioxide in air. The results of the potentiometric determination of nitrite using the present electrode were compared with those results obtained from standard spectrophotometric method [19].

Determination of Nitrite in Water and Soil Samples. Table IV shows the results obtained for determination of nitrite in water and soil samples spiked with a known amount of nitrite. The nitrite concentration was determined using nitrite-CMCPE applying the standard addition method. As can be seen from the results, it is immediately obvious that in all cases, there is a satisfactory agreement between the results obtained by the present potentiometric method and the standard spectrophotometric method (recovery ranges 98–99 %). The potentiometric method, however, offers the advantages of simplicity, applicability to turbid solutions and sensitivity.

Table III: Comparison of the performance characteristics of the nitrite-chemically modified carbon paste electrode with previously reported nitrite electrodes.

Ion-recognition	Slope (mV)	Detection limit (mol·L ⁻¹)	Linear range (mol L ⁻¹)	Response time (s)	Interfering ions	Ref.
Vitamin B12	-58.2	1.9×10 ⁻⁵	4.0×10 ⁻⁵ – 1.0×10 ⁻¹	2–7	not reported	2
Butylphthalocyaninecobalt	-57.0	1.0×10 ⁻⁵	1.0×10 ⁻⁵ – 1.0×10 ⁻¹	20–120	not reported	3
Axially mono coordinated Co(III)-porphyrin	-58.4	8.0×10 ⁻⁶	1.0×10 ⁻⁶ – 1.0×10 ⁻¹	few seconds	SCN ⁻	14
Cobalt phthalocyanine	-52.0	1.0×10 ⁻⁷	5.0×10 ⁻⁶ – 6.0×10 ⁻²	–	not reported	36
Tetraphenyl-porphyrinato) Co(III) chloride + TDMAC	-58.4	1.0×10 ⁻⁵	1.0×10 ⁻⁵ – 1.0×10 ⁻¹	–	SCN ⁻ , ClO ₄ ⁻	4
Rhodium(III) 5,10,15,20-tetra(<i>p</i> -tertbutylphenyl)-porphyrin chloride	-62.1	5.0×10 ⁻⁶	1.0×10 ⁻⁵ – 1.0×10 ⁻²	180	not reported	5
Uranyl salophen	-56.2	–	1.0×10 ⁻³ – 1.0×10 ⁻¹	–	ClO ₄ ⁻	6
Co(II)-salophen complex	-59.8	8.0×10 ⁻⁷	1.0×10 ⁻⁶ – 1.0×10 ⁻¹	<10	not reported	7
Cobalt(II)-salen + HTAB	-58.2	5.0×10 ⁻⁷	1.0×10 ⁻⁶ – 1.0×10 ⁻¹	10	not reported	8
Octakis(benzylthio)-tetraazaporphyrin Co (III)	-30.0	1.0×10 ⁻⁶	1.0×10 ⁻⁵ – 1.0×10 ⁻¹	13	Cl ⁻ , S ²⁻	9
Co-benzopyran-4-one Schiff base	-60.3	7.0×10 ⁻⁶	9.1×10 ⁻⁶ – 1.5×10 ⁻²	20	SCN ⁻	this work

Determination of Nitrogen Dioxide in Air. Several methods have been used for the measurement of nitrogen dioxide in the ambient air. In urban air, the chemiluminescence method has replaced the manual absorption solution methods, and is introduced as an ISO standard [40]. The chemiluminescence method for NO₂ is based on reduction to NO by a heated catalytic converter and calculation of the concentration as the difference between mixture (NO + NO₂) and NO alone (the signal without converter). Also, the liquid phase

NO₂-luminol chemiluminescence reaction has been used in a commercial monitor for nitrogen dioxide at low levels [41]. This monitor has been shown to give almost interference-free values for NO₂ [42].

Table IV: *Determination of nitrite in water and soil samples using nitrite-chemically modified carbon paste electrode.*

Sample	Spiked with (µg·ml⁻¹)	Nitrite-CMCPE (µg·ml⁻¹)	RSD (%)	Spectrophotometric method (µg·ml⁻¹)	Recovery (%)
Water samples					
Mineral water	1.0	1.110	0.30	1.120	99.10
Water (El-Warrak)	1.0	1.130	0.57	1.120	99.10
Water (Giza)	1.0	1.136	0.40	1.135	100.08
Soil samples					
Soil (New Cairo District)	1.0	1.156	0.50	1.153	100.26
Soil (Cairo University)	1.0	1.200	0.45	1.220	98.36
Soil (Sixth October)	1.0	1.212	0.37	1.199	101.08

The manual absorbing solution method based on direct Griess reaction during sampling has also been appointed as ISO standard [43]. This method is sensitive and more selective than the chemiluminescence method, but the color to be measured spectrophotometrically is developed during sampling, and the measurements have to be performed immediately after sampling due to instability. Thus, this makes the method unsuitable if the exposed absorbing solution has to be transported to a chemical laboratory far from the sampling site, particular if temperature and light exposure cannot be controlled. Other solutions have been used in which nitrogen dioxide is absorbed and transformed to nitrite [44]. These methods are usually not sensitive enough in background areas, and also have the problem of instability of the exposed absorption solution during transport when the temperature and sunlight cannot be controlled.

A method based on absorption of nitrogen dioxide on a sodium iodide impregnated glass-sinter has been developed by Ferm and Sjodin [45]. This method is recommended at European Monitoring and Evaluation Programme (EMEP) stations with low concentrations of NO₂ and where the analysis has to be performed in a laboratory far from the sampling site. Ambient air with a flow rate of 0.5 L·min⁻¹ is drawn through an air intake (inverted funnel)

and a glass filter impregnated with sodium iodide (NaI) and sodium hydroxide (NaOH). Nitrogen dioxide is absorbed in the filter and the iodide reduces NO_2 to nitrite (NO_2^-). The hydroxide is converted to carbonate during sampling due to the uptake of carbon dioxide. The nitrite formed on the glass filter is extracted with deionized water. After extraction the nitrite concentration can be determined by ion chromatography.

Table V: *Determination of nitrogen dioxide in air samples using nitrite-chemically modified carbon paste electrode.*

Sample	Nitrite-CMCPE ($\mu\text{g}\cdot\text{m}^{-3}$)	RSD (%)	IC method ($\mu\text{g}\cdot\text{m}^{-3}$)	Recovery (%)
Air 1 (Shoubra)	0.525	0.40	0.537	97.77
Air 2 (Shoubra)	2.060	0.50	2.082	98.94
Air 3 (Shoubra)	3.050	0.37	3.120	97.75

In the present application (Table V), the ion chromatographic measurements were replaced by potentiometric measurements of nitrite using the nitrite-CMCP electrode. The samples of analysis of this application were kindly provided by the Center of Environmental Hazards Mitigation (CEHM) at Cairo University. This method can be used for measurement of nitrogen dioxide on a 24 h basis in an ambient air within the range of 4–10 $\mu\text{g}\cdot\text{m}^{-3}$ NO_2 and also in urban air up to 300 $\mu\text{g}\cdot\text{m}^{-3}$ NO_2 (air sample of 0.7 m^3). Exposed samples are stable for several weeks and can be transferred to the laboratory for chemical analysis. The extraction volume may be adjusted according to the concentration level expected. At sites of low NO_2 concentrations, an extraction volume of about 5 mL has found to be appropriate. In urban air measurements the sample may be extracted with a volume of 10 mL or even larger. The large extraction volume facilitates the potentiometric measurements based on nitrite chemically modified carbon paste electrode. As can be seen from the results (Table V) there is a good agreement between the results obtained by the present potentiometric method and the standard ion chromatographic method (recovery ranges 97–99 %). The potentiometric method, however, offers the advantages of simplicity, rapidity, applicability to turbid solutions, application in situ and sensitivity.

Potentiometric Titrations. In contrast to direct potentiometry, the potentiometric titration technique usually offers the advantage of high accuracy and precision. A further advantage is that the potential break at the titration end-point must be well defined, but the response of the

used electrode needs to be neither reproducible nor Nernstian, and the actual potential value at the end point is of secondary interest. In these titrations, the nitrite-CMCPE was used as an indicator electrode for the titration of 0.138, 0.230, 0.322, and 0.460 mg of NaNO₂ against standard silver nitrate solution. The potential jumps at the vicinity of end point, ranges from 50–100 mV for titration of 0.138 to 0.460 mg nitrite with percent recovery ranges from 92–100 %. The results reflect a very high degree of completeness of the titration reactions.

Statistical Treatment of Results. The calculated F values [46] were less than the tabulated F value (6.39) where $\nu_1 = 4$ and $\nu_2 = 4$ at 95% confidence level. T-test [46] was also performed at 99.9% confidence level (tabulated t = 8.61), the results are shown in Table VI. The method applied with the use of the constructed electrode does not exhibit significant differences in comparison with the official method which reflects the accuracy and precision of this method.

Table VI: *Statistical treatment of data obtained for the determination of nitrite using nitrite-CMCP electrode in pure and real samples in comparison with the official spectrophotometric and ion chromatographic (IC) methods.*

Sample	Spectrophotometric or IC	Nitrite-CMCP electrode	F-test	T-test
Pure solution	99.90	99.00	1.12	0.21
Tap water	99.80	99.10	1.01	0.15
Soil (Cairo University)	99.50	98.36	1.03	0.23
Air sample	99.00	97.70	1.05	0.94

Conclusion

In the field of ion-selective electrodes applied for determination of anions, the aforementioned results have clearly demonstrated the significant advantages of using chemically modified carbon paste electrode in potentiometric assay of anions. In this study, the proposed chemically modified carbon paste electrode based on new Co(III)-benzopyran-4-one Schiff base complex electrode is found to be an efficient nitrite-selective sensor and can be used for determination of this ion in the presence of considerable concentrations of different common anions. Notably, the low detection limit, and the wide concentration range of the proposed sensor are attractive properties to be the sensor of choice for nitrite determinations in many real life samples.

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