



A new thin film modified glassy carbon electrode based on melaminium chloride pentachlorocuprate(II) for selective determination of nitrate in water

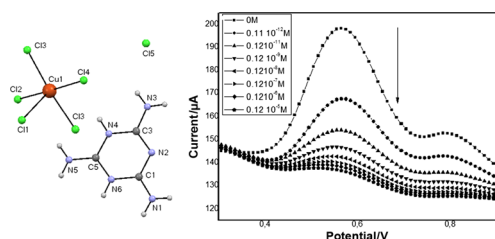
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Abstract

A new electrochemical thin film glassy carbon sensor for nitrate detection based on a copper complex, namely melaminium chloride pentachlorocuprate ($\text{H}_2\text{mela})\text{ClCuCl}_5$ (mela = melamine), as a novel ionophore in plasticized polyvinyl chloride matrix was elaborated. The title complex was synthesized and characterized using FT-IR spectroscopy and single-crystal X-ray diffraction. To improve the sensitivity, the optimal pH value was evaluated and the effect of plasticizer was performed using three different plasticizing solvent mediators: dioctyl sebacate, dibutyl phthalate, and *o*-nitrophenyl octyl ether. The optimum performance was observed at pH 4 with the membrane incorporating dioctyl sebacate as a plasticizer. Cyclic voltammetry and square wave voltammetry were used to characterize the $(\text{H}_2\text{mela})[\text{CuCl}_5]\text{Cl}$ -GC sensor with a potential between 0.3 and 1 V. This sensor was characterized by a wide linear range from 1.2×10^{-10} M to 1.2×10^{-7} M, a low limit of detection of 1.2×10^{-10} M and low response time less than 1 min. This proposed sensor gave good results in the determination of nitrate in water and, therefore, can be used successfully in real samples.

Graphic abstract



Keywords Electrochemical sensor · Glassy carbon electrode · Melaminium chloride pentachlorocuprate(II) ionophore · Nitrate · Cyclic voltammetry · Square wave voltammetry

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Introduction

The development of chemical sensors is currently one of the most active areas of analytical research. Sensors are small devices that incorporate a recognition element with a signal transducer. Such devices can be used for direct measurement of the analyte in the sample matrix. There are a variety of combinations of recognition elements and signal transducers [1]. Recently, the utility of chemical sensors in industry has increased due to the rapid growth of environmental concern. For instance, nitrates, phosphates, and heavy metals constitute frequent pollutants of superficial and ground waters [2–4].

Electrochemical (voltammetric) detection with ion-selective electrodes (ISEs) can be considered as an advantageous analytical method. Consequently, considerable efforts have been devoted to the construction of ISEs that function on the basis of chemical recognition principle because of their ability to translate the chemistry of new substrate-binding systems into tools that can be applied in the selective recognition of various target species in the presence of potentially interfering analytes. The recognition elements which can be utilized in the selection of suitable carriers for construction of ISE should have a suitable size and a specific metal–ligand interaction [5]. The development of novel chemical sensors is closely related to the synthesis of new materials such as conjugated polymers and ionophores [6].

Anion receptors or ionophores are an important field of increasing research in supramolecular chemistry [7]. These molecules have recently attracted a lot of interest because they are making the detection of new analytes accessible, allowing comprehensive instrumental control over sensing characteristics and introducing new detection principles [8, 9]. Most prepared anion receptors based on the principle of hydrogen bonding, hydrophobic, electrostatic, and anion– π interactions are being developed for anion coordination [10–15]. The most utilized groups for the purpose of anion binding by hydrogen bonds are amide, thioamide, urea, thiourea, and amine functions [7, 16].

Environmentally, nitrate anions constitute a large proportion of current pollutants that cause «eutrophication» of rivers, leading to algal blooms and becoming a serious problem [17].

Considerable efforts have been devoted to the detection of NO_3^- , especially in water because of its high toxicity and wide spread in the environment. Several nitrate-selective electrodes based on anion exchangers, such as quaternary ammonium salts [18–20], phosphonium salts [21, 22] and metallated organic ligands [23, 24] have been reported.

In this perspective, organic–inorganic salts based on melaminium cations could be considered as potential anion receptors. Furthermore, the protonated and

non-protonated forms of this molecule represent good building blocks for constructing supramolecular architectures [25, 26], because of the presence of hydrogen-bonding sites and the formation of various protonated forms which can act as hydrogen-bonding acceptors [27]. Melamine has also been used to construct supramolecular architectures with phosphate [28], sulfate [29] and carboxylate anions [30].

The main aim of this work is to design a melamine derivative molecule in a highly selective membrane electrode with good response characteristics. In this sense, melaminium chloride pentachlorocuprate ($\text{H}_2\text{mela})\text{ClCuCl}_5$ was synthesized. Fully characterized using FT-IR spectroscopy and single-crystal X-ray diffraction and explored as a potential ionophore for the construction of PVC-based polymeric membrane for selective determination of NO_3^- ions on glassy carbon electrode. Cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques were used for the characterization of this sensor.

Results and discussion

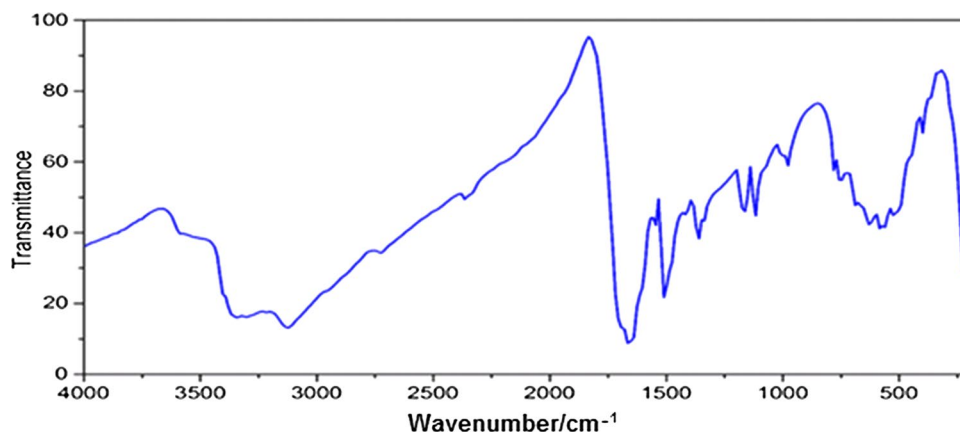
Band assignments

The FT-IR spectrum of the melaminium chloride pentachlorocuprate is reported in Fig. 1. The different vibrational frequencies observed in the FT-IR spectrum of the title compound along with corresponding bands' assignments are given in Table 1 and are based on a comparison of the IR spectra of other melaminium-containing compounds [31–34].

The 4000–3500 cm^{-1} region consists of two IR absorption bands characteristic of the $-\text{NH}_2$ groups belonging to the melamine cation as well as the two $-\text{NH}^+$ groups of the triazine ring [35–37]. Thus, the absorption band at 3350 cm^{-1} is assigned to the $\nu_{\text{as}}(\text{N-H})$ asymmetric stretching, whereas the absorption observed at 3127 cm^{-1} results from the $\nu_{\text{s}}(\text{N-H})$ symmetric stretching.

Moreover, two other characteristic N–H vibrations appear at 1694 cm^{-1} and 1664 cm^{-1} and could be attributed to the $\delta(\text{N-H})$ bending modes (asymmetric and symmetric, respectively). Those broad bands are shifted to higher frequencies compared to other similar melamine derivatives (usually 1670 and 1600 cm^{-1} , respectively) indicating that those groups are involved in the formation of hydrogen bonds [38] of different strengths. This agrees with the observations of H-bonds in the crystal structure of the title compound elucidated by means of the single-crystals' X-ray diffraction results [27].

The vibrations region under 350 cm^{-1} can be assigned according to chlorocuprates(II)-containing compounds from the literature [39, 40]. Therefore, the band observed

Fig. 1 FT-IR spectrum of (H₂mela)ClCuCl₅**Table 1** FT-IR absorption bands assignment for the title compound

Absorption/cm ⁻¹	Bands vibration
3350 (s, br)	$\nu_{as}(\text{N-H})$ asymmetric stretching
3127 (s, br)	$\nu_s(\text{N-H})$ symmetric stretching
1694 (vs, br)	$\delta_{as}(\text{N-H})$ asymmetric bending
1664 (vs, br)	$\delta_s(\text{N-H})$ symmetric bending
1503 (s, sh)	$\nu_{as}(\text{C-N})$ asymmetric stretching of the side groups
1365 (m, sh)	$\nu(\text{C=N})$ stretching of the ring
1167 (m, sh)	$\nu_s(\text{C-N})$ symmetric stretching of the side groups
1116 (m, sh)	$\rho(\text{N-H})$ rocking of the side groups
982 (w, sh)	Triazine ring vibration
230 (vs, sh)	$\nu(\text{Cu-Cl})$ stretching

at 230 cm⁻¹ originates from the copper–chlorine stretching mode associated with the Cu–Cl bonds [35, 41, 42].

The data obtained from FT-IR spectroscopy agree perfectly with the results of the X-ray diffraction analysis of the melamine salts based on a series of inorganic acids (melaminium sulfate [43], melaminium tetrachlorocuprate [44], etc.) and organic acids (melaminium tartrate [45], melaminium bis(hydrogen oxalate) [46], melamine pyromellitic acid [47], 4-hydroxybenzenesulfonate [48], etc.). These salts are characterized by the formation of deprotonated melaminium cations (the melamine is protonated at two nitrogen atoms of the triazine ring). In all cases, the melaminium cations and the organic/inorganic anions are joined together by means of hydrogen-bonding interactions.

Single-crystal X-ray diffraction

Experimental conditions used for the single-crystal data collection are reported in Table 2. The unit cell determination and data reduction were performed using the CrysAlis program [49]. A total of 8961 reflections were collected, of which 2855 were independent and 2044 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods using the program

Table 2 Crystal and experimental data

$\text{C}_3\text{H}_8\text{Cl}_6\text{CuN}_6$	$Z=4$
$M_r=266.27$	$F(000)=534$
Monoclinic, $P2_1/m$	$D_x=2.018 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation, $\lambda=0.71073 \text{ \AA}$	$\theta=3.6\text{--}31.8^\circ$
$a=5.6947(6) \text{ \AA}$	$\mu=2.18 \text{ mm}^{-1}$
$b=14.9784(14) \text{ \AA}$	$T=170 \text{ K}$
$c=10.2898(11) \text{ \AA}$	$\beta=93.089(9)^\circ$
$V=876.42(16) \text{ \AA}^3$	$0.1 \times 0.15 \times 0.15 \text{ mm}^3$
8961 measured reflections	$h=-8 \rightarrow 8$
2855 independent reflections	$k=-21 \rightarrow 21$
2044 reflections with $I > 2\sigma(I)$	$l=-8 \rightarrow 15$
$R_{\text{int}}=0.052$	Least-squares matrix: full
Refinement on F^2	$S=0.99$
$R[F^2 > 2\sigma(F^2)]=0.033$	$w=1/[\sigma^2(F_o^2)+(0.0355P)^2]$
$wR(F^2)=0.078$	where $P=(F_o^2+2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}=0.003$	$\Delta\rho_{\text{max}}=0.86 \text{ e \AA}^{-3}$
2855 Reflections	$\Delta\rho_{\text{min}}=-0.61 \text{ e \AA}^{-3}$
121 Parameters	

SIR2008 [50] and refined by full-matrix least-squares technique on F^2 including all reflections with SHELXL-2013 program [51]. Both softwares were included within the WingX crystallographic software package [52]. The refinements converged at conventional R factor of 0.033 and wR of 7.8%. Maximum and minimum peaks in the final difference Fourier syntheses were 0.86 and -0.61 e \AA^{-3} . Structural representation of the complex was drawn using MERCURY [53] (Fig. 2).

Optimization of experimental conditions

Effect of pH

Since an acidic environment is required for the detection of nitrate, it is important to study the relationship between the

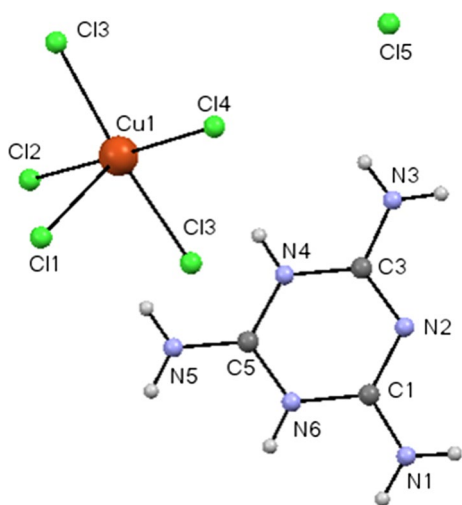
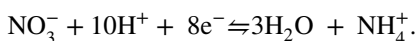


Fig. 2 Structural representation of melaminium chloride pentachlorocuprate used as the carrier in the PVC membrane

peak current and the pH value. As seen from Fig. 3, when the $(\text{H}_2\text{mela})\text{ClCuCl}_5\text{-GC}$ sensor was placed in electrolytes of different pH values (2, 3, 4, 5 and 6 were adjusted by 2 M H_2SO_4), the peak current varied with the pH but reached a maximum at pH 4. This may be attributed to the reduction of nitrates also requiring the presence of protons as they yield to the formation of NH_2OH or NH_3 in accordance with the following equation [54]:



As the above equation shows an acidic environment is required because hydrogen ions make the formation of NH_2OH or NH_3 possible. However, the onset of hydrogen evolution at low pH values may interfere with the nitrate

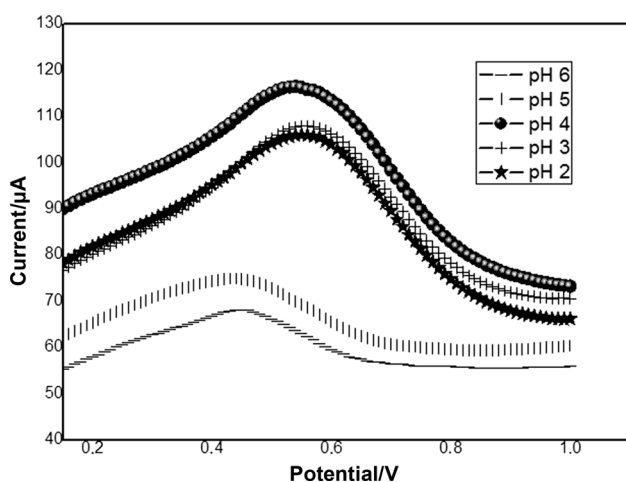


Fig. 3 pH Optimization of $(\text{H}_2\text{mela})\text{ClCuCl}_5\text{-GC}$ sensor

electro-reduction as both occur at similar potentials, so it is very important to choose the suitable pH value [55, 56]. The result also shows that the acidity of the supporting electrolyte will affect the peak current and the peak shape too.

Effect of the plasticizer

It is well established that the plasticizer plays a vital role in the sensor performance as it is responsible for the ionophore solvation and distribution in the membrane matrix, thus controlling the detection limit [57] and affecting the selectivity and sensitivity [58].

The membrane sensor incorporated melaminium chloride pentachlorocuprate complex as an anion carrier as well as dioctyl sebacate (DOS) as a plasticizer. The membrane compositions and response characteristics of these sensors are summarized in Table 3.

The influence of the plasticizer type on the characteristics of the $(\text{H}_2\text{mela})\text{ClCuCl}_5\text{-GC}$ sensor was investigated using three plasticizers with different polarities and lipophilicities including dibutyl phthalate (DBP, $\epsilon_r = 6.4$, $\log P_{\text{TLC}} = 4.45$), DOS ($\epsilon_r = 3.9$, $\log P_{\text{TLC}} = 10.2$) and *o*-nitrophenyl octyl ether (NPOE, $\epsilon_r = 23.9$, $\log P_{\text{TLC}} = 5.9$).

The plasticizer DOS produced the maximum sensitivity for all the plasticizers. The $(\text{H}_2\text{mela})\text{ClCuCl}_5\text{-GC}$ sensor containing DOS showed better voltammetric responses, i.e., better sensitivity and linearity of the calibration plots. It seems that DOS as a low polarity compound among the plasticizers investigated provides more appropriate conditions for the incorporation of the nitrate ions into the membrane. The sensor-incorporated DOS as plasticizer had the lowest limit of detection (LOD). This is due to the fact that the membrane does not reach the minimum polarity required for improving the mobility and diffusion of active centers, which is impeded at the same time, as a result of high lipophilicity of the employed plasticizer [59].

It is to be noticed that the observed poor sensitivity for the electrode plasticized using NPOE results from the high dielectric constant which has a negative effect on the extraction of nitrate ions [60]. Consequently, we used DOS as the plasticizer in the following experiments.

Table 3 Limit of detection (LOD) and linear range values of the nitrate-GC sensor with different plasticizers

Plasticizer	Correlation coefficient	Linear range/ <i>M</i>	Detection limit/ <i>M</i>
DOS	0.99	1.2×10^{-10} to 1.2×10^{-7}	1.2×10^{-10}
DBP	0.98	1.2×10^{-8} to 1.2×10^{-6}	1.2×10^{-8}
NPOE	0.94	1.2×10^{-9} to 1.2×10^{-7}	1.2×10^{-9}

Linear range and limit of detection of the sensor under the optimum condition

Under the optimum condition, the relationship between the peak current and the ion concentration was studied. The peak current decreases with the increase of the concentration of nitrate (Fig. 4). The reduction peak potential of nitrate was between 0.4 and 0.8 V and the peak potential does not vary with the variation of the concentration. The second peak at about 0.8 V corresponds to the reduction of nitrite [61, 62].

Moreover, the calibration curve shows that a good linear correlation ($R^2=0.99$) can be observed. The limit of detection calculated from the parameters obtained reached 1.2×10^{-10} M and the result exhibits, therefore, more simplicity and sensitivity of this method.

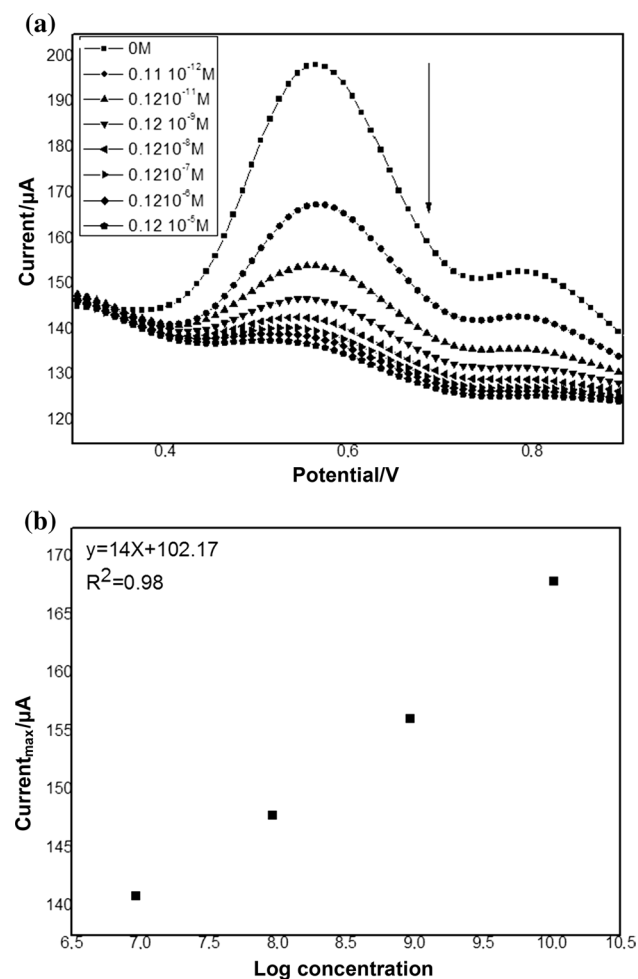


Fig. 4 **a** Typical SWV curves of the (H₂mela)ClCuCl₅⁻ GC sensor in response to varying concentrations of nitrates in sodium acetate/ acetic acid buffer solution at pH 4; **b** the corresponding calibration plot of peak currents

Comparison of linear range and LOD of (H₂mela) ClCuCl₅⁻ GC sensor with literature values

The linear range and LOD of (H₂mela)ClCuCl₅⁻ GC sensor were compared with the values reported in the literature (Table 4). As it can be seen, the sensor shows a lower limit of detection of about 1.2×10^{-10} M with a linear range of 1.2×10^{-10} – 1.2×10^{-7} M toward NO₃⁻. Our sensor is found to be better than the other sensors with regard to both the linearity range and the lower minimum detection limit value.

Study of interferences

For voltammetric determination of nitrate in water, there are always some common inorganic ions in water samples considered as possible interferences to NO₃⁻. The (H₂mela) ClCuCl₅⁻ GC sensor response toward Cl⁻, SO₄²⁻, and H₂PO₄⁻ at pH 4 is studied using SWV method. NO₃⁻, Cl⁻, SO₄²⁻, and H₂PO₄⁻ were prepared in buffer sodium acetate/ acetic acid over a wide concentration range of 0.11×10^{-12} M – 0.12×10^{-5} M at pH 4 under stirring (Table 5). The calibration curves (Fig. 5) of the (H₂mela)ClCuCl₅⁻ GC sensor for NO₃⁻, Cl⁻, SO₄²⁻, and H₂PO₄⁻ ions were obtained from voltammetric response.

From these results we can deduce that the affinity to the (H₂mela)[CuCl₅]Cl was less for most of these interfering elements except in the case of NO₃⁻ which seems to have a higher affinity, because it showed the best linear range and the highest sensitivity. It is worth noted that the selectivity coefficient (log *K*) was calculated according to [67].

Analytical application

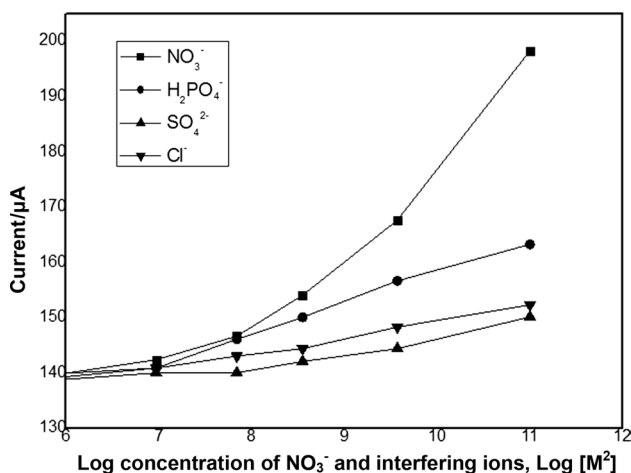
Various types of water samples were subjected to the detection of NO₃⁻ in water with the help of the newly fabricated sensor after addition of buffer (sodium acetate/ acetic acid) and pH adjustment (pH 4) [68]. The city of Khenchela (East of Algeria) was selected for testing the new nitrate-selective sensor. Three real samples were selected with initial concentrations of nitrate ions determined by the spectrophotometric method. The limit of detection and the linear range of (H₂mela)ClCuCl₅⁻ GC sensor in different water samples

Table 4 Limit of detection (LOD) and linear range of the nitrate-GC sensor compared with the literature values

Reference	Linear range/M	Detection limit/M
[63]	5×10^{-6} to 1×10^{-1}	2.5×10^{-6}
[64]	1×10^{-5} to 1×10^{-1}	2.3×10^{-5}
[65]	1×10^{-5} to 1×10^{-1}	1.9×10^{-6}
[66]	7.5×10^{-7} to 1×10^{-1}	2×10^{-8}
This work	1.2×10^{-10} to 1.2×10^{-7}	1.2×10^{-10}

Table 5 Analytical properties of (H₂mela)ClCuCl₅⁻ GC sensor for interfering elements

Analyte	Sensitivity/ μA	Log <i>K</i>	Linear range/ <i>M</i>	Detection limit/ <i>M</i>	Correlation coefficient
NO ₃ ⁻	14.00	0	1.2 × 10 ⁻¹⁰ to 1.2 × 10 ⁻⁷	1.2 × 10 ⁻¹⁰	0.99
H ₂ PO ₄ ⁻	5.61	-0.3971	1.2 × 10 ⁻⁹ to 1.2 × 10 ⁻⁷	1.2 × 10 ⁻⁹	0.98
SO ₄ ²⁻	2.59	-0.7328	1.2 × 10 ⁻⁸ to 1.2 × 10 ⁻⁶	1.2 × 10 ⁻⁸	0.97
Cl ⁻	2.89	-0.6852	1.2 × 10 ⁻⁹ to 1.2 × 10 ⁻⁷	1.2 × 10 ⁻⁹	0.96

**Fig. 5** Response of the (H₂mela)ClCuCl₅⁻ GC sensor for NO₃⁻ over H₂PO₄⁻, SO₄²⁻ and Cl⁻ in sodium acetate/acetic acid buffer solution at pH 4

were studied and compared with its detection in aqueous solution. The results summarized in Table 6 clearly show that the stripping of NO₃⁻ in the real samples occurs effectively at the (H₂mela)ClCuCl₅⁻ GC sensor.

Conclusion

In this work, a new nitrate-selective electrode based on a melaminium chloride pentachlorocuprate(II) (H₂mela)ClCuCl₅(mela = melamine) as a novel ionophore was studied using cyclic voltammetry (CV) and square wave voltammetry (SWV). The optimal pH value was evaluated and the effect of plasticizer was performed using three different plasticizing solvent mediators DOS, DBP and NPOE.

Table 6 Limit of detection (LOD) and linear range of the (H₂mela)₂CuCl₆⁻ GC sensor of different real water samples collected from three different river sites in Khenchela

River area	Correlation coefficient	Linear range/ <i>M</i>	Detection limit/ <i>M</i>
Hammam Essalihine	0.98	1.1 × 10 ⁻¹¹ to 1.2 × 10 ⁻⁹	1.1 × 10 ⁻¹¹
Ain Mimoun	0.98	1.2 × 10 ⁻⁸ to 1.2 × 10 ⁻⁶	1.2 × 10 ⁻⁸
Bouhmama	0.98	1.2 × 10 ⁻⁹ to 1.2 × 10 ⁻⁵	1.2 × 10 ⁻⁹
Aqueous solution	0.99	1.2 × 10 ⁻¹⁰ to 1.2 × 10 ⁻⁷	1.2 × 10 ⁻¹⁰

On the basis of the results discussed in this work, the sensor incorporating DOS as plasticizer displayed a linear response for NO₃⁻ ions in a wide concentration range of 1.2 × 10⁻¹⁰ to 1.2 × 10⁻⁷ M. The sensor was found to perform satisfactorily in pH 4. The comparison of this sensor and the literature showed that the (H₂mela)ClCuCl₅⁻ GC sensor is superior to the reported ones in terms of wider linear concentration range and lower detection limit. The response of our sensor toward NO₃⁻ ions is better than that of the required values of Cl⁻, SO₄²⁻, and H₂PO₄⁻. Therefore, melaminium chloride pentachlorocuprate complex as a novel ionophore can be considered as a carrier for the construction of a novel PVC-based membrane for nitrate detection in water.

Experimental

For membrane preparation, high-molecular weight polyvinyl chloride (PVC), dibutyl phthalate (DBP), dioctyl sebacate (DOS), *o*-nitrophenyl octyl ether (*o*-NPOE), and tetrahydrofuran (THF) were used as received from Fluka. Melamine from Sigma-Aldrich was used to synthesize the ionophore as described below. The test solution was prepared by dissolving the nitrate salts in sodium acetate/acetic acid buffer solution.

Synthesis of the ionophore (H₂mela)[CuCl₅]Cl

Following a new procedure different from the one previously reported [27], the title compound was synthesized by preparing separately a hot ethanol–water solution (1:1, 10 cm³, 60 °C) of melamine (1.5 mmol) and an aqueous solution (10 cm³) of CuCl₂·2H₂O (3 mmol). The metallic salt solution

was then added dropwise to the hot melamine solution in a 2:1 molar ratio and stirred for 30 min until an almost clear solution was obtained. After cooling the resulting mixture to room temperature, it was filtered out to remove any amount of insoluble material and then kept to evaporate at room temperature to finally lead to the growth of brown bloc-like crystals after several weeks. The crystals of the title compound were then collected and dried in air.

FT-IR measurements

The FT-IR spectrum of the title compound was recorded in the range of 200–4000 cm^{-1} , using KBr pellet with a PerkinElmer FT-IR spectrophotometer at room temperature.

Single-crystal X-ray diffraction

The X-ray single-crystal structure of the title compound was determined by mounting a dark brown block-like crystal on an Oxford Diffraction Xcalibur CCD diffractometer with a fine-focus sealed tube graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) using φ and ω scans at 170 K in the range of $3.6 \leq \theta \leq 31.8^\circ$.

Preparation of the membrane

The PVC-based membrane was prepared by dissolving 33 mg of PVC, 67 mg of the plasticizer (DOS), and 4 mg of melaminium chloride pentachlorocuprate ($\text{H}_2\text{mela}[\text{CuCl}_5]\text{Cl}$) in 3 cm^3 THF. For the optimization of the plasticizer, we used two others in the membrane DBP (dibutyl phthalate) and NPOE (*o*-nitrophenyl octyl ether) with 67 mg for each one.

Preparation of the electrode

Prior to the determination, glassy carbon electrode (GCE) was manually polished with alumina powder (Al_2O_3 , size 0.05 μm) until a mirror surface was obtained. After that the electrode was left in acetone for 5 min and in Piranha (mixture of 2/3 sulfuric acid and 1/3 oxygenated water H_2O_2) for 2 min, to further eliminate microparticles absorbed on the electrode surface. 15 mm^3 of the prepared membrane was deposited on the surface of the glassy carbon electrode and then left dried in open air for 12 h. Cyclic voltammetry was used to characterize the surface of the GCE using a potential from -0.8 to 0.8 V in potassium ferricyanide/ferrocyanide solution.

Electrochemical measurements

Electrochemical measurements were carried out using an EC-lab SP 300 with a conventional three electrodes system; modified glassy electrode, platinum wire and saturated calomel electrode were used as the working, auxiliary and reference electrodes, respectively and inside a Faraday cage. Electrochemical measurements were performed at ambient temperature ($25 \pm 1^\circ\text{C}$) using a 7110 pH meter (Inolab) (2 M) sulfuric acid for pH control and with an Orion Ag/AgCl double-junction electrode. Square wave voltammetric measurements were run from 0.3 to 1 V, scan rate 100 mV s^{-1} , using an electrochemical cell with 30 cm^3 containing a three electrode system.

Analytical application

In terms of sampling, water samples were collected from three selected river areas in Khenchela, namely, Bouhmama, Ain Mimoun and Hammam Essalihine. For comparative purposes, KNO_3 standards at concentrations of 1, 2, 3, 4, and 5 mg/dm^3 were prepared and the absorbance at these concentrations was taken. A plot of average absorbance versus concentration in mg/dm^3 is shown as the standard calibration curve in Fig. 5. This standard graph was used to estimate the nitrate concentration of samples at any given absorbance.

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