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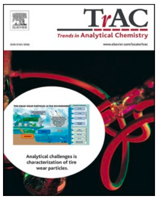

Trends in nitrite detection: Recent advances in electrochemical sensor technologies

Július Gajdár [a,c], Sara Rodrigues Gaspar [a,c], M. Gabriela Almeida [a,b,c,*]

[a] UCIBIO – Applied Molecular Biosciences Unit, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516, Monte de Caparica, Portugal
[b] Centro de investigação interdisciplinar Egas Moniz (CiiEM), Egas Moniz School of Health and Science, Campus Universitário, Quinta da Granja, 2829-511, Caparica, Portugal
[c] Nitrogen Sensing Solutions Lda, Leiria, Portugal

ABSTRACT

Nitrite has become increasingly significant analyte in analytical chemistry, with its monitoring being essential in various industrial sectors, environmental studies, and healthcare applications. The importance of nitrite detection is evident in the growing number of research publications focused on this topic in recent years. This review specifically concentrates on the development and application of electrochemical sensors. Herein, we provide a comprehensive overview of the methodologies used for nitrite determination, including approaches based on nitrite reduction and oxidation, as well as the use of nitrite biosensors and potentiometric sensors. We attempt to highlight the progress and innovations made in this field since 2010, aiming to give readers a broad understanding of the current state of research and its future directions.

1. Introduction

The nitrite ion (NO_2^-) is a simple molecule that significantly impacts the environment and human welfare. Its effects have garnered global attention from the scientific community and government authorities due to the potential health hazards caused by human exposure to high nitrite concentrations, such as the increased risk of carcinoma [1,2], nitrosative stress [3], and methemoglobinemia, also known as blue baby syndrome [4].

One significant source of exposure is the use of nitrite as a food preservative in the form of sodium salt ($NaNO_2$). In addition to preventing bacterial proliferation, it imparts a bright pink colour to meat products. It is also used in animal feed, and fishmeal, thus appearing in the human food chain. Naturally, the presence of nitrite in green leafy vegetables, some tubers, and fruits is low (less than 100 mg kg^{-1}), but the massive usage of nitrogen-based fertilizers can raise the nitrite content significantly. Modern farming practices can also contribute to the dysregulation of the biogeochemical *N*-cycle, leading to the contamination of surface water, and soils with its intermediate products [2,3,5,6]. The activity of *Nitrosomonas* bacteria, for instance, is augmented, thereby enhancing the nitrite levels. Noteworthy, a study from Sebilo found that only 60 % of the applied N-fertilizers were taken up by plants, while the rest remained in the soil and leaked into the nearby water bodies even 30 years after fertilization [7]. Farming fields near water bodies are thus sources of contamination, extensively affecting the aquatic ecosystems. In addition, bacterial activity can also convert nitrate into nitrite in stagnant waters containing this nutrient under oxygen-poor conditions. The cycle of nitrogen in nature with its sources and transformations is illustrated in Fig. 1.

The normal concentration of nitrite in groundwater supplies is around 0.3 mg L^{-1}. Higher levels may lead to water contamination, which puts potable water sources and aquatic life in danger. The maximum admissible level of nitrite ions in drinking water given by the WHO guidelines is 3 mg L^{-1} [6]. Recently, the European Food Safety Authority (EFSA) published a comprehensive issue regarding the risk assessment of nitrate and nitrite in animal feed with maximum amount of permitted nitrite as an additive in 180–500 mg kg^{-1} range [8]. Therefore, it is extremely important to monitor the nitrite levels in water, soil, foodstuff, feeding, and biological samples, as demonstrated by the remarkable increase in the annual publication of research papers over the past 13 years, with the number more than doubling in 2023 compared to 2010 (from ~80 papers per year to ~160). Our literature survey is illustrated in Fig. 2. Approximately half of these research papers are related to electrochemical sensing and biosensing. We have identified several less common electrochemical methods with only a few numbers of papers (“other” in Fig. 2). We considered them too sparse to

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[*] Corresponding author. UCIBIO – Applied Molecular Biosciences Unit, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516, Monte de Caparica, Portugal.

E-mail address: mg.almeida@fct.unl.pt (M.G. Almeida).

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be discussed in detail in this review. These methods include coulometry [9], electronic tongue analysis system [10], electrochemiluminescence [11], capacitance [12], and photoelectrochemistry [13]. Other approaches for nitrite detection include optical methods (including the Griess method), and separation (hyphenated) techniques. Nitrite concentrations are commonly denominated either in (μ)mol L^{-1} (more common for chemists), in ppm/mg L^{-1} of nitrite anion and in ppm/mg L^{-1} of nitrite-nitrogen. We included Table 1 to facilitate this conversion for readers.

For many years, the most common and widely used methodology for nitrite detection and quantification was the Griess method. It was developed in the 19th century and is still the topic of many research papers (see Fig. 2). The Griess method uses a colourimetric reaction to specifically quantify nitrite using spectrophotometry [14]. Other approaches based on optical methods include the development of novel colourimetric or fluorescent probes, and methods based on UV–Vis, and Raman spectroscopy [14,15].

Detection by separation methods includes the use of ion chromatography, liquid chromatography (HPLC), gas chromatography (GC) or electrophoresis [16,17]. In comparison with electrochemical methods, these methods generally provide more accurate results, with lower detection limits, and they are superior in the analysis of complex matrices. However, significant disadvantages are associated with bench methodologies. For instance, they are time-consuming, require high reagent volumes, use bulky technical apparatus, and sometimes specialist technicians to operate the equipment. According to today's demands for quick decision-making, it is crucial to opt for new approaches that allow real-time and point-of-need nitrite analysis. From this viewpoint, the electrochemical techniques provide very convenient solutions. The key advantages of electrochemical systems include the speed of measurement, low cost, little to no reagents necessary, possibility of miniaturization and portability, scalability, and capability of remote operation. In the case of electrochemical sensors and biosensors, they can be selective, work in a wider range of concentrations, they are not affected by the turbidity of a sample, and provide highly sensitive responses [18]. Therefore, they are the focus of this review.

Given the abundance of available references on this important subject, we selected, critically evaluated, and highlighted those papers that offer novel and interesting solutions in nitrite analysis, thereby contributing to a broader understanding of the topic. In addition, we aim to offer practical guidelines for the scientific community, addressing prevalent issues such as inaccuracies, incomplete data, and the absence of crucial experimental conditions that we have encountered during our review process.

2. Voltammetric and amperometric techniques

This section is devoted to electrochemical sensors based on voltammetric and amperometric techniques. Amperometry (also called chronoamperometry) involves biasing the potential of the working electrode to a set value and monitoring the current-time dependence. The obtained current value should change depending on the analyte concentration. The selectivity of the method depends on the chosen detection potential as a lower potential is more selective (less prone to interferences from other compounds in a sample) while a higher potential is less discriminating. Voltammetric methods involve sweeping the potential at the working electrode and monitoring current-potential dependence. Potential sweeping can be either linear, in linear sweep voltammetry, or rendered with pulses, in differential pulse or square-wave voltammetry; these methods differ by the pulse waveform and sampling procedure. The resulting peak-shaped voltammograms can be evaluated and depend on the analyte concentration. Pulse techniques are more selective compared to amperometry as multiple species can be differentiated based on the peak position, however, they are more demanding about instrumentation and the peak evaluation is more complex [18].

Nitrite can be detected by these methods either by following its reduction or oxidation, as described in the following subsections (Fig. 3).

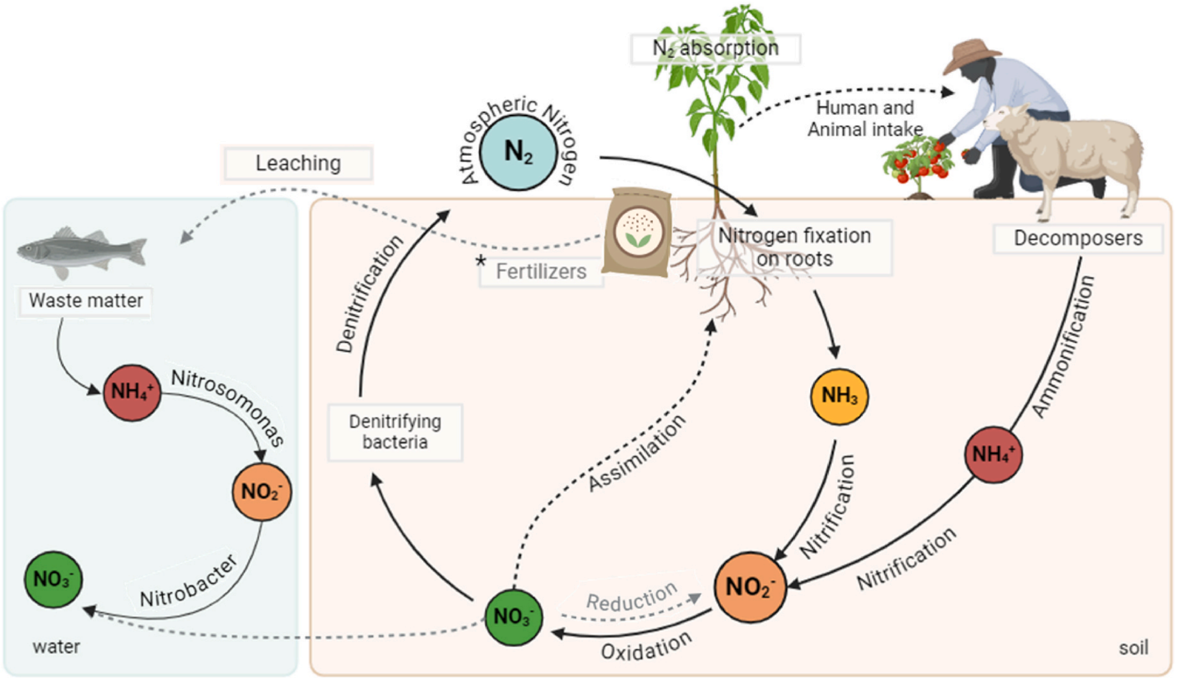

Fig. 1. The nitrogen cycle is a biogeochemical process that describes the transformation and movement of nitrogen through the atmosphere, soil, water, and living organisms. The cycle involves multiple stages – such as nitrogen fixation by plants, nitrification, assimilation, ammonification, and denitrification – through which nitrogen is converted into different chemical forms. These processes enable the incorporation of nitrogen into biological systems, supporting the growth and functioning of ecosystems. However, human activities (highlighted with * in the figure) have contributed to the unbalance of the *N*-cycle, particularly through excessive use of nitrogen-based fertilizers leading to their leaching into nearby water bodies. This contributes to increased levels of ammonia, nitrates, and nitrites in the environment.

2.1. Methods based on nitrite reduction

Nitrite can be reduced at the electrode according to the following global reaction (eq. (1)), which mechanism may vary based on the material used:

$$NO_2^- + 8H^+ + 6e^- \rightarrow NH_4^+ + 2H_2O \qquad \text{Eq. 1}$$

Considering this reaction, sensors based on reduction should theoretically be more sensitive based on the exchange of 6 electrons compared to the only 2 that are exchanged during oxidation (Eq. (2)). However, the detection of nitrite by its reduction has fewer publications compared to other methods, with only around 60 articles out of a total of approximately 900 (see Fig. 2). Two main problems must be considered when sensing nitrite this way. Firstly, the reduction potential of nitrite is very negative, and a suitable electrode modification or electrode pretreatment is crucial for achieving good results. Secondly, the biggest practical obstacle in the on-site application of these methods is the oxygen reduction reaction. While oxygen depletion is typically done in the lab by purging the solutions with an inert gas, such as nitrogen or argon, this is difficult for on-site applications. There are three main strategies to address this issue, namely, i) to use an oxygen scavenging system, ii) design a way to shift the potential of analyte reduction to more positive values, or iii) develop a material that increases the overpotential of oxygen reduction [19,20]. This information must be included in the manuscript, yet the authors fail to provide these details in some cases. Hence, we are left to make assumptions about whether the oxygen removal actually took place. Other possible important interferents are nitrates (NO_3^-), as they usually accompany nitrites in samples. Less common interferents that are either very specific to the studied sample or have more negative (uncatalyzed) reduction potential, may be also a matter of concern. These include metallic ions with lower reduction potential such as Fe^{3+}, Pb^{2+}, Cu^{2+}, heavy metals; sulphites (SO_3^{2-}), peroxides, thiocyanides SCN^-, cyanides CN^-, halogen-containing anions such as chlorides Cl^- or chlorates ClO_3^-. Basic information about selected papers is shown in Table 2.

Copper is the most commonly used material for nitrite reduction as it was proven to effectively catalyse the reaction [21,22]. The reduction potential was reported between 0 to −0.2 V (vs Ag/AgCl/1 M KCl; denoted hereafter simply as Ag/AgCl). However, an activation of this copper surface must be performed before the measurement. The activation process involved copper dissolution and redeposition, which creates a rough surface that is essential for nitrite reduction. Gamboa et al. have explained the mechanism of copper activation that is related to nitrite reduction mechanism. They have also developed a simple copper electrode sensor that can detect nitrite in mineral water and rainwater by differential pulse voltammetry (DPV) [22]. Copper can also be deposited on the electrode in the form of nanoparticles. They were shown to further enhance the analytical signal, thanks to the increase in the active area [23]. These approaches had a drawback as they required an acidic environment, and no signal was obtained for a pH higher than 3. This is because the reaction requires eight protons and there is a significant change in peak potential with varying pH. Therefore, a robust procedure to monitor and control pH would be necessary for these sensors.

Table 1
Concentration conversion table for nitrite, assuming the density of a solution is 1 g mL^{-1}.

c, μM	c(NO_2), mg L^{-1}	c(NO_2–N), mg L^{-1}
1	0.046	0.014
21.74	1	0.304
71.43	3.286	1

Another promising new group of materials that were investigated to electrocatalytically reduce nitrite were polyoxometalates (POMs). A material based on multiple layers of Dawson-type tungstophosphate $K_7[H_4PW_{18}O_{62}]\cdot 18H_2O$ (PW_{18}) was reported to detect nitrite at low potentials around −0.3 V (vs Ag/AgCl) in acidic solutions. This material had no significant response to oxygen at nitrite detection potential. An amperometric sensor based on this POM was developed and applied in samples of drinking water, showing stability over a 2-month period [24].

Amperometric sensors can be based on rhodium Rh(III) complex on multi-wall carbon nanotubes on a glassy carbon electrode (MWCNT/GCE) [25], or Fe_3O_4 nanoparticles on graphene sheets [26]. The reduction potential is around −0.4/−0.5 V (vs Ag/AgCl) and the detection was again carried out at acidic pH in an anoxic environment (oxygen had to be nitrogen purged beforehand). These sensors were proven to be reasonably sensitive, and stable.

Detection at neutral pH was carried out using a composite electrode with platinum nanoparticles co-deposited with thionine and MWCNT on a gold electrode. The reduction occurred at approx. −0.6 V (vs Ag/AgCl) with a repeatable response when used daily for four weeks [27].

Reduction can also be observed on boron-doped diamond (BDD)

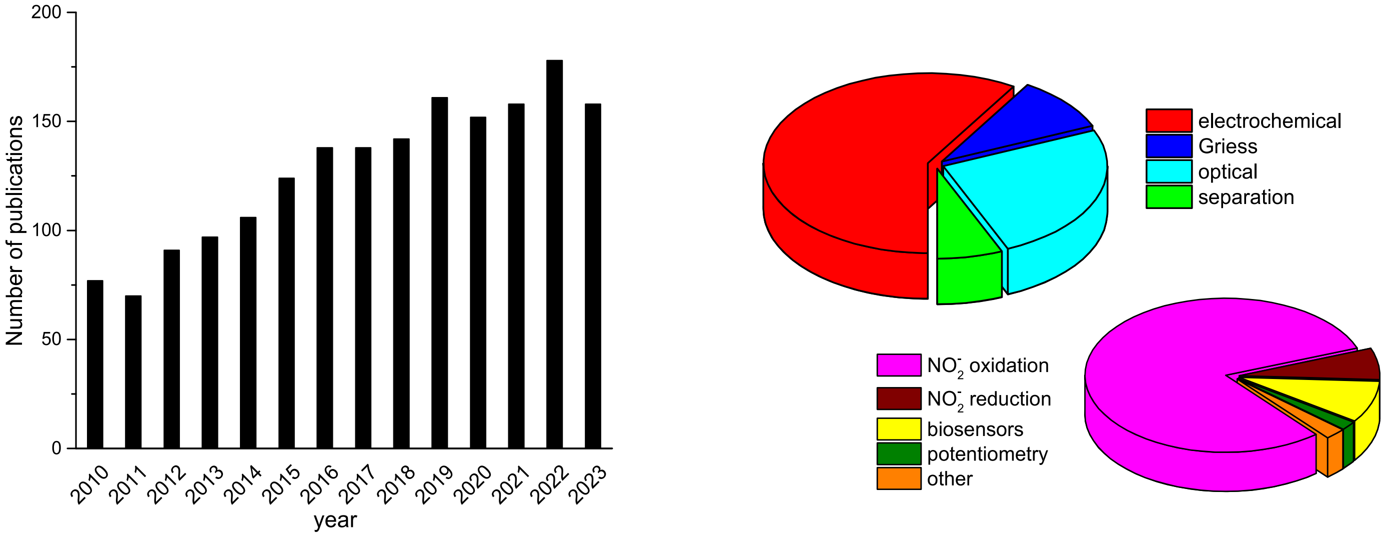

Fig. 2. The number of publications related to nitrite sensing organized by the year of publication since 2010 and by the used analytical method (sub-divided further in the case of electrochemical methods). A publication search was carried out in the Web of Science database using the search phrase: "nitrite" detection OR sensor OR determination. Only relevant papers were manually selected.

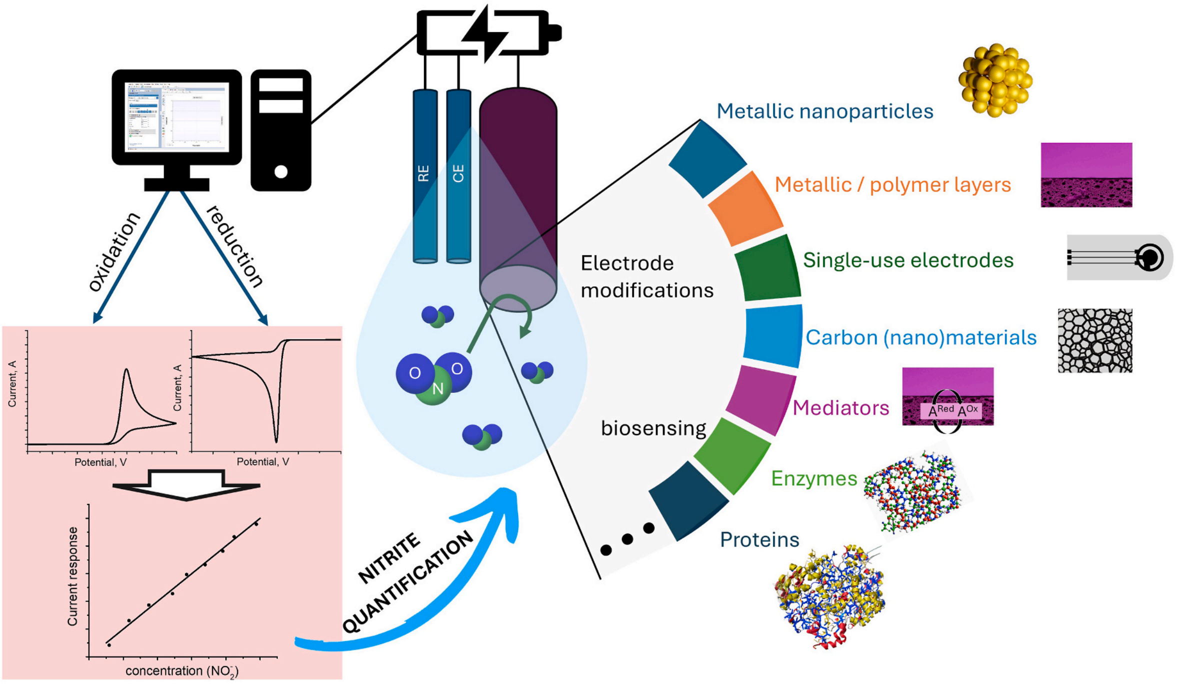

Fig. 3. Schematic of voltammetric/amperometric nitrite sensors and most common surface modifications of working electrode surface.

Table 2
Selected works on nitrite detection by reduction.

electrode	technique	conditions	O_2 removal	LOD, μM	LDR, μM	Type of real sample	Ref.
Bare copper	DPV	pH 2	N_2 purge	0.17	0.17–100	Natural water	[21]
Cu/MWCNT/RGO/GCE	SWV	pH 3	Not specified	0.03	0.1–75	Foodstuff, water samples	[23]
POM/GCE	Amp	pH 1.2	Not necessary	0.1	0.1–20000	Tap water	[24]
Rh-complex/MWCNT/GCE	Amp	pH 2	N_2 purge	0.08	0.25–10	Salami	[25]
PtNP/TH/MWCNT	CV	pH 7	N_2 purge	0.2	0.5–150	–	[27]
BDD	DPV	pH 6	N_2 purge	18	10–8000	Urine	[28]
PB/CPE	Amp	pH 1	Not necessary	9	25–1000	Water samples, sausage	[29]

electrodes as recently shown by Zhang et al. These electrodes provided a wide potential window and resistance to non-specific adsorption. The reduction potential was observed around −0.9 V, but even at this very negative potential, the sensor was performing well in urine samples, thanks to the lack of interference in this matrix [28].

Nitrite reduction can be mediated using chemical mediators such as the $[Fe(CN)_6]^{3-/4-}$ couple (Prussian blue, PB) immobilized in a carbon paste electrode. Nitrite additions provided an increase in cathodic current. The detection was performed at a very low potential of +0.2 V (vs Ag/AgCl), and no interference from oxygen, nitrate, or sulphite was observed [29].

2.2. Methods based on nitrite oxidation

The reaction for nitrite oxidation can be simply expressed as:

$$NO_2^- - 2e^- + H_2O \rightarrow NO_3^- + 2H^+ \qquad \text{Eq. 2}$$

The reversibility of this reaction depends on the electrode material used. It is irreversible on glassy carbon, quasi-reversible on pyrolytic graphite, and reversible on gold. In comparison to reduction, this reaction is almost unaffected by pH, unless there are no other processes occurring, as no protons are necessary for the reaction. However, nitrite can be protonated to HNO_2 at pH around its pK_a of 3.4, which then changes the oxidation mechanism [30].

Nitrite detection by oxidation looks to be much more favourable (see Fig. 2) considering the large number of papers in this area (approx. 750). This can be explained by the lack of oxygen interference, making it simpler to implement. Another reason for so many papers is that thanks to its simple reaction, nitrite is widely used as an electrochemical probe to test novel electrode materials, ranging from carbon-based electrodes to metal electrodes including both conventional and less conventional metallic surfaces and their chemical modifications, as well as polymeric composites. The justification for the high number of papers on the development of these new electrode materials is the aim to i) Improve electrode kinetics and lower the oxidation potential, which then improves the selectivity of the method. ii) Improve analytical response, which leads to higher peak current (or area) or amperometric current, resulting in better sensitivity, limit of detection (LOD), and linear dynamic range (LDR). iii) Improve selectivity by using the specific binding of the analyte to a surface. iv) Prevent fouling effects of the electrode surface that degrade analytical response over time. v) Increase the shelf life of the material, making it more suitable for on-site analysis or for developing commercial solutions [31]. The following subsections discuss many different approaches that differ in the nature of the electrode material and the complexity of its preparation (for a short overview of selected papers, see Table 3).

Generally, despite the wide variety of complex composite materials and nanomaterials presented so far, most of them exhibit a similar oxidation potential compared to simpler electrode configurations, with the oxidation peak (or detection potential in amperometry) in the range of 0.7–0.8 V (vs Ag/AgCl). This potential is often too positive for practical applications because many organic and inorganic molecules may also give a response in this region. Common interferences with nitrite

Table 3
Selected works on nitrite detection by oxidation.

electrode	technique	conditions	LOD, μM	LDR, μM	Type of real sample	Ref.
GCE	Amp	pH 3	0.4	2.5–10	–	[38]
N-RGO	Amp	pH 7	0.2	0.5–5000	Juice, garlic, river water	[41]
Carbon fibre μ-elode	Amp	pH 7	5.5	6–2000	Saliva, tap water	[42]
Carbon paper	Amp	pH 7	0.07	0.1–3838	Sausage, mineral water	[43]
G-PLA (3D print)	DPV	pH 2	0.03	0.5–250	Urine, saliva	[45]
NPG Au	Amp	pH 7.4	0.01	1–100	Sausage, water samples	[50]
AuNP/f-MWCNT/LIG	SWV	pH 6	0.9	10–140	Tap water	[51]
AgNP/P(MMA-co-AMPS)	Amp	pH 7	0.2	$1–10^5$	Tap water	[55]
Cu nanoporous/GN/GCE	Amp	pH 9	0.009	0.1–100	Water samples, sausage	[57]
Pt black	Amp (FIA)	pH 7.4	0.01	0.01–1000	–	[59]
Fe_2O_3-RGO	DPV	pH 7	0.015	0.05–780	Tap water	[66]
MnO_2/GO-SPE	DPV	pH 7.4	0.09	0.1–1; 1-1000	Water samples	[67]
MoS_2/RGO/PEDOT	DPV	pH 4	0.059	1–1000	Water samples, milk	[72]
Pd/GCM	Amp (FIA)	pH 5	0.03	0.1–4000	Gunshot residue	[74]
CS@PB/GNS-CNS	Amp	pH 2	0.001	0.002–390	Sausage	[77]
Ni_7S_6/MWCNT	amp	pH 13	0.3	1–4200	Water samples	[78]
Au–Pd/RGO	Amp.	pH 7	0.02	0.05–1000	Tap water	[80]
Fe_2O_3 NP/Cu-BDC MOF/SPE	Amp	pH 7	0.07	1–2000	Water samples	[82]
FeSe/CC	Amp	pH 7	0.07	0.7–240	Pickled vegetable	[84]
$K_3[Fe(CN)_6]$-PDDA-Alg/Au	Amp	pH 0.3	0.07	5–9700	River water	[85]
AuNP/graphene/PAD	DPV	pH 4.75	0.1	0.3–720	Water samples, sewage, milk	[87]
Graphite SPE	CV	pH 7	15.1	100–1000	Canal water	[88]

oxidation might include sulphide, sulphite, nitrate, chloride, ascorbic acid, dopamine, uric acid, hydroquinone, catechol, and most phenolic or polyphenolic compounds. Yet, some authors often select interferents that are unlikely to cause interference, as they cannot be easily oxidized, such as metallic ions (e.g., Ca^{2+}, Cu^{2+}, Na^{+}, Mg^{2+}) or hydrogen peroxide, and fail to test the above-mentioned oxidizable compounds, leading to incorrect claims about the selectivity of their sensor. Therefore, more innovative work is needed to increase the selectivity of nitrite detection. In our opinion, many studies used nitrite primarily as a probe or model analyte, with the focus being more on the electrode material itself rather than on nitrite electrochemical sensors.

One of the options to discriminate the response of nitrite in complex matrices is the employment of techniques like DPV or SWV. For instance, nitrite was detected together with hydroquinone, catechol, and p-cresol as they can coexist in biological fluids on MWCNT-modified RGO material [32], and similarly on MWCNT-modified CTAB-functionalized GO [33].

2.2.1. *Carbon-based electrodes*

Carbon electrodes, such as screen-printed electrodes, carbon fibres, carbon paper or conductive polymers with carbon can be considered simple and cheap sensors, making them ideal for on-site applications. Recently, the use of carbon nanotubes for nitrite detection was summarized in a review by Cho et al. [34], while another review by Li et al. focused on graphene-based materials [35], and a review by Li et al. concentrated on carbon nanomaterials [36]. Composite materials based on graphene for nitrite detection were reviewed by Marlinda et al. [37].

Nitrite oxidation can be observed on electrode materials without any modification, with only a simple pre-treatment of the surface. The unnecessity of electrode modification for the detection of nitrite was explained in detail by Kozub et al. at unmodified glassy carbon electrode with a detection potential around 0.8 V [38].

A simple homemade carbon ink electrode is a perfect example of a low-cost sensor that is easily fabricated. For example, Petroni et al. made a mixture of graphite and polystyrene, using SWV for the detection. This technique showed no interference for nitrite detection at an otherwise very positive potential of 1.0 V [39]. Similarly, this very positive detection potential was required for an amperometric sensor based on a graphite electrode presented for urine nitrification monitoring. Although this detection potential and higher LOD (100 μM) were more than suitable for their study, it might not be sensitive enough for other applications [40].

A lower oxidation potential (~0.65 V vs Ag/AgCl) with carbon materials was achieved by Chen et al. on a nitrogen-doped graphene-oxide-based sensor [41]. The introduction of nitrogen improved the conductivity and facilitated the charge transfer (about 100 mV shift). The sensor proved to have an excellent LDR (0.5–5000 μM) with a LOD of 0.2 μM. Since carbon surfaces are prone to fouling, pulsed amperometry can be used to improve the performance. In the case of a carbon fibre microelectrode reported by Saraiva et al., reactivation consisted of imposing a short pulse at optimized potential values to achieve a stable long-term amperometric response [42].

Recently, carbon fibre paper has received considerable attention in the electrochemical field due to its good conductivity, large surface area, and good mechanical properties. In the work by Zhu et al. carbon paper was at first annealed, which increased edge sites, introduced oxygen groups, and improved wettability, ultimately enhancing the oxidation response of nitrite with a very low LOD of 0.07 μM [43]. Another source of carbon material, biochar, can be obtained from natural sources and biomass by pyrolysis. Deposition of biochar from waste material on SPE enhanced the response of the electrode with about a 100 mV shift in potential, in a work by Ferlazzo et al. [44].

With the recent growth of 3D printing technologies and the development of conductive polymers, a 3D-printed graphene/polylactic acid electrode was introduced for the detection of nitrite. The printed electrode had to be polished and treated with a solvent before use. It was shown to perform well in urine and saliva samples, although detection was carried out at 1.0 V, making the method less selective [45]. This technology promises the production of sensors on a large scale, custom size (made for purpose) and with reduced production costs.

Composite carbon electrodes are one of the small modifications of carbon material that can improve some characteristics. This is the case of a combination of graphite, polypyrrole and chitosan proposed by Ye et al. based on chitosan's NH_3^+ attraction of nitrite anions. Nevertheless, only about 30 mV shift was observed compared to GCE [46].

2.2.2. *Metallic electrodes, gold, silver, copper, and platinum*

Gold, silver, copper, and platinum are some of the most commonly used metals for modifying electrodes to detect nitrite. Nitrite detection on gold nanomaterials was reviewed by Saha et al. [47] and detection on noble metals in two reviews by Yang [48] and Zhang [49].

The studies in which sensors are modified by gold differ in the variety of electrode or nanoparticle preparation, their shape and size, as well as the preparation of composites with one or more metals. One of the novel materials presented was nanoporous gold, which was prepared by Kumar et al. through the electrodeposition of $AuCl_4^-$ solution onto a gold substrate [50]. A 100 mV shift of nitrite peak was observed compared to the bare gold (0.77 V) and increased the intensity of the CV wave about two times. A remarkably sensitive sensor was reported by Nasraoui et al., which was based on laser-induced graphene patterned on a flexible polyimide substrate and modified with COOH functionalized MWCNT and gold nanoparticles prepared by drop casting. Their modification decreased the oxidation potential to 0.62 V, with both MWCNT and AuNP contributing to the effect. The preparation of the sensor was reproducible with an error of less than 3 % [51]. A novel integrated gold mini sensor based on a silica chip is a good example of a sensor that can be mass-produced by microfabrication for commercial use. Although this sensor provided acceptable stability and response consistency, it had a relatively high LOD of 500 μM [52]. However, Wang et al. found out, contrary to other publications, that there was no electrocatalytic effect of nanoparticles for the oxidation of nitrite when comparing gold nanoparticles and gold macroelectrode [53]. Although most studies compare modified materials to substrates that might not be bulk gold (i.e. glassy carbon), Wang et al. observed an increase in current with higher coverage of nanoparticles, but no potential shift could be observed. These findings were additionally confirmed by computational studies.

Silver and silver nanoparticles are another popular material among electrochemists due to their catalytic effects, relatively stable nanoparticles, and lower cost. In a study by Pal and Ganesan [54], silver nanoparticles anchored to silica spheres were characterized and then deposited on a glassy carbon electrode. Three oxidation peaks were observed that corresponded to the catalysis of nitrite oxidation mediated by silver oxidation. The first peak, observed at 0.4 V (vs Ag/AgCl), could be used to construct a calibration plot in two LDRs (10–80 and 80–300 μM). However, the sensor's response was not stable after more than a week. In another study by Rastogi et al. [55], silver nanoparticles were incorporated into a copolymer and characterized. Three oxidation peaks were observed corresponding to nitrite oxidation with the first peak occurring at 0.3 V (vs SCE). The process was found to be electrochemically irreversible. Nitrite detection was carried out at a potential of 0.9 V with an excellent LDR and reproducibility (3.9 % in electrode preparation).

Copper is used as an electrode material for both the oxidation and reduction of nitrite. Compared to noble metals like Au, Ag, and Pt, copper is more cost-effective, has high catalytic potential and good electrical conductivity. However, copper nanoparticles are easily oxidized by air, which makes them unstable over the long term. Manoj et al. claimed that this problem could be solved by preparing stable Cu nanoparticles dispersed with MWCNT and using them in the amperometric nitrite detection. Nitrite oxidation was observed in one peak at 0.93 V (vs SCE) with a considerable current increase compared to bare MWCNT. The sensor provided a stable response for at least 3 weeks [56]. Nanoporous materials provide a high surface-to-volume ratio and significantly improve reaction kinetics thanks to a high number of active sites; for this reason, a copper nanoporous material was prepared for nitrite oxidation by Majidi and Ghaderi. The preparation procedure was carried out with hydrogen bubbles formed during electrodeposition to create a 3D structure on a graphene nanosheet substrate. The detection was carried out by amperometry at 0.8 V (vs SCE). The electrode was stable for at least 5 days [57]. Copper in a different state than metallic (0) has also been used in ionic forms (I, II), avoiding the problem of copper(0) oxidation. For instance, a novel and environmentally friendly material called biochar was prepared from waste eggshell membrane with adsorbed Cu^{2+} from wastewater, turning it into a sensing device. Pyrolysis of this material yielded biochar enhanced with copper ions, which is sensitive to nitrite oxidation at 0.75 V (vs Ag/AgCl) in an amperometric sensor [58].

Platinum is another widely used electrode material, but the high cost is its biggest disadvantage. Despite being considered an inert metal, nitrite oxidation on the platinum surface is limited due to the poisoning effects. To overcome this, a platinum black electrode was used in a microfluidic device. This electrode has the advantage of high surface area and together with flow conditions that help with the sensitivity (as the mass transport is enhanced) minimized inhibition effects compared to Pt bulk electrode. Detection was performed by amperometry at 0.85 V (vs Ag/AgCl) [59]. Platinum nanowire networks have been reported to have higher sensitivity than platinum black, with a peak potential of 0.7 V (vs SCE). However, it also experienced poisoning effects, which can be eliminated by treating the electrode with sulphuric acid [60]. An alloy material made of Pt and CoO has been found to eliminate poisoning effects and reduce the content of Pt, leading to a lower price of electrode material [61].

2.2.3. Other metal-based materials

The development of improved materials for electrochemical sensors also includes metals (or their derivatives) that are less traditional in electrochemistry. Examples of these metals include cobalt, iron, manganese, molybdenum, nickel, palladium, titanium, ruthenium, zinc, and others. Iron-based composites were closely reviewed in a paper by Li et al. [62].

A few examples of this are sensors based on metal oxides such as Co_3O_4 [63–65], Fe_2O_3 [66], MnO_2 [67,68], NiO [69], $Ni(OH)_2$ [70], and In_2O_3 [71]. They were studied for their catalytic characteristics; they are environmentally friendly, they provide good material stability, and their availability and cost are usually better than rare metals. The preparation can involve drop-casting or incorporation into carbon ink. Some oxides, though, have lower electrical conductivity and therefore, this must be overcome during the electrode preparation through for example, mixing with more conductive materials. The main advantage was the increase in the current response as the peak potential (or detection potential) was not outstanding compared to other materials. Regardless, there were some exceptions. For example, the Co_3O_4/RGO electrode had a lower peak potential of 0.54 V (vs SCE) at very alkaline conditions [64]. The reported oxidation potential on MnO_2 was also low, around 0.55 V, but it must be mentioned that the reference here was a screen-printed Ag/AgCl paste, which is just a pseudo-reference electrode [67]. In contrast, a composite material based on $MnO_2@C_3N_4$ with a true Ag/AgCl reference exhibited nitrite oxidation around 0.8 V [68].

Another interesting material is MoS_2 nanoparticles with reports of excellent catalytic activity and low cost. However, MoS_2 are poorly conductive, and hence they must be formed in a composite, for example, with PEDOT and RGO [72], or a carbon nanomaterial made from cellulose [73]. The nitrite peak was observed at 0.9 V (vs SCE) but the current was mainly enhanced thanks to the increase of active surface area.

Palladium nanoparticles have also been studied for nitrite detection. These nanoparticles provide excellent chemical stability and catalytic activity. In an application-focused research paper, a composite of palladium particles and glassy carbon microspheres was used to detect gunshot residue in a flow amperometric detection. Nitrite ions are generated after gunpowder combustion. The detection potential was 0.9 V (vs Ag/AgCl) and the main advantage was a higher surface area, which improved the LOD down to 30 nM. The electrode provided excellent stability with the ability to perform more than 200 measurements in series. The analysis was performed in gunshot residue samples, and no interference was observed in this matrix [74]. Doping of the nitrogen-doped graphene as a substrate material with palladium nanoparticles was claimed to improve electrocatalytic performance and improve stability. Nitrites were detected at 0.77 V (vs SCE), with improvement over bare GCE [75]. A composite of Pd, Fe_2O_3 nanoparticles and graphene was also used for nitrite sensing with a peak at 0.8 V (vs SCE) for the analysis of decomposing vegetables [76].

Remarkably, a low LOD was reported in a work based on chitosan coated Prussian blue nanoparticles with a mixture of graphene nanosheets and carbon nanospheres, where Prussian blue nanoparticles were claimed to act as a redox mediator. Although the detection potential was not improved (0.86 V vs SCE), the LOD value was as low as 1 nM [77]. Interestingly, the catalysis of nitrite oxidation was observed with a three-dimensional network consisting of Ni_7S_6 and multi-walled carbon nanotubes, a material applied in batteries, catalysts, electrochromic and solar energy devices. The oxidation potential was decreased to 0.45 V (vs Ag/AgCl) and the reaction was reversible, but the sensor was operated in very alkaline conditions (pH 13). The sensor showed good stability for at least 30 days [78].

It has been reported that a suitable combination of nanoparticles can have a synergistic effect that significantly improves nitrite sensing. For instance, a sensor based on Au and Co_3O_4 nanoparticles showed good reproducibility and applicability for real matrices. Nonetheless, the oxidation potential (0.75 V vs Ag/AgCl) was not greatly improved [79]. Similarly, it has been claimed that bimetallic Au–Pd alloy nanostructures could have a catalytic effect. The amperometric detection was carried out at 0.85 V (vs Ag/AgCl), with LOD of 20 nM and wide LDR (50 nM–1 mM) compared to most materials [80].

Metal-organic frameworks (MOF) as an electrode material offer a large surface area, are easy to synthesize and can be fine-tuned for specific applications by changing metal composition. As the common MOFs suffer from poor electron mediation and low stability, novel composite materials have been receiving more attention. A recent review by Yang et al. summarized the use of MOFs for nitrite detection [81]. For example, a combination of copper-based MOF and Fe_2O_3 was reported to catalyse nitrite oxidation using amperometric detection at a moderately low potential of 0.5 V (vs Ag/AgCl) with acceptable repeatability and long-term stability of the material itself [82]. A thin film of MOF and graphene nanoribbon composite material gave a peak at 0.8 V (vs Ag/AgCl) while a composite with Ag and halloysite nanotubes (a naturally available clay mineral) exhibited oxidation potential at 0.75 V (vs Ag/AgCl) [83]. Another promising electrode material was the low-cost and well-conductive metal selenides. Nanomaterials based on FeSe, for instance, have a large surface area, good conductivity, and excellent stability and reproducibility [84].

An amperometric nitrite sensor can be also based on a redox mediator such as $K_3[Fe(CN)_6]$ immobilized in poly(diallyldimethylammonium)-alginate composite. Nitrite oxidation was facilitated via the redox mediator, which shifted the detection potential to 0.2 V (vs SCE). However, the pH of the solution had to be acidic as a neutral pH yields no electrocatalytic response [85].

An approach based on the development of a portable smartphone-based electrochemical system for nitrite sensing was presented by Xu et al. They developed a low-cost sensing system consisting of tools and Android software that can automatically detect, report, and share results. Their device can detect nitrite levels using modified SPE and produce results comparable to standard laboratory electrochemical instrumentation [86].

2.2.4. *Single-use electrodes*

Paper-based devices recently captured the attention of electrochemistry owing to their low price and convenience, as well as their advantages as disposable electrodes. Traditional sensors are sensitive to electrode fouling over time and have poor sensitivity in complex matrices. These disposable single-use devices do not suffer from these problems, making them more applicable for on-site applications. A paper-based device with a gold nanoparticle/graphene working electrode was found to catalyse nitrite oxidation comparably to bulk electrode systems [87]. Another paper-based SPE with a graphite working electrode was able to detect nitrite around the potential of 1.0 V, but this high potential is prone to interferences. Although the manufacturing was reproducible, the sensor was not applicable for the sensitive detection of low concentrations. Nevertheless, the advantages of screen printing on different base materials provide low cost, high reproducibility, and high-volume production [88]. Another case of a SPE nitrite sensor was developed based on Mn_3O_4 microcubes and graphene sheets, presented as low-cost and abundant materials. The electrode was reported to be specific to nitrite while common interferents like ascorbic acid or dopamine were not detected [89]. Additionally, gold nanoparticles/ERGO composite can also be prepared as an SPE, combining the catalytic effect of gold with the advantages of the disposable sensor. This amperometric sensor operating at 0.65 V (vs Ag/AgCl paste RE) had good accuracy and repeatability [90].

2.3. *Electrochemical biosensors*

Biosensors emerged as advanced point-of-care devices, offering high sensitivity and specificity for molecular detection. They integrate a bioreceptor that interacts with the analyte and a transducer that converts this biorecognition event into a measurable signal. This biosensing element must be firmly attached to the substrate electrode, which can be achieved through various methods: adsorption (enzyme immobilization), covalent bonding (creating chemical bonds between the side chains of biomolecules and the substrate), entrapment in a suitable polymer, or encapsulation in a membrane. In some cases, a mediator is necessary to facilitate the electron transfer. Biosensors can be classified based on the type of bioreceptor or transducer used. A recent review paper summarized enzyme-based biosensors for nitrite analysis [91]. Generally, biorecognition elements are categorized into two groups: non-specific proteins and nitrite reductases. Additionally, recent studies have explored the use of whole bacteria in biosensing. There are approximately 85 papers on this topic, with the majority (65) focusing on non-specific proteins (see Fig. 2 and Table 4).

2.3.1. *Bacteria-based biosensors*

In recent years, several studies have reported the use of electroactive bacterial biofilms in the design of electrochemical biosensors to monitor aquatic pollutants such as nitrite. For example, Wang et al. utilized a mixed population of nitrite-oxidizing bacteria (NOB), which contain nitrite oxidoreductase (NXR) that oxidizes nitrite to nitrate, as the biological element. The preparation of the biofilm on the electrode required considerable time, with a 10-day acclimation period on the electrode surface. Using CV, nitrite was detected at +0.6 V (vs. Ag/AgCl) with LOD of 0.28 μM. However, the presence of heavy metals was found to potentially impact the metabolic activity of the bacteria [91]. Another recent study investigated a mixed population of nitrite-reducing

Table 4
Selected works on biosensors for nitrite quantification.

biosensor	technique	LOD, μM	LDR, μM	Type of real sample	ref
NOB	CV	0.28	21.4–5700	Water samples	[91]
NRB	LSV	2.0	2–320	Wastewater	[92]
SOD	CV	0.05	0.1–1000	Plasma, whole blood, saliva	[93]
HRP	Amp	0.21	1–5400	Water samples	[94]
Cyt-c	Amp	0.5	10–100	–	[95]
Hb	Amp	0.1	0.1–2000	Sausage	[99]
Mb	SWV	0.95	0.5–5000	Meat products	[101]
Cu-NiR	Amp	0.06	0.06–18	–	[102]
ccNiR	CV	4.7	5–50	Urine	[105]

electroactive bacteria as the biological component of the sensor. In this case, the biofilm took 6 days to develop on a graphite sheet electrode. The sensor's response to nitrite occurred at −0.5 V (vs. Ag/AgCl) with an LOD of 2 μM. The authors emphasized the biosensor's capability for continuous operation with minimal change in response over 8 days [92]. However, these types of biosensors still face challenges in terms of sensitivity, selectivity, and response time compared to enzymatic biosensors.

2.3.2. *Biosensors based on non-specific protein*

Several non-specific proteins, such as cytochrome *c*, horseradish peroxidase/catalase (HRP), superoxide dismutase (SOD) [93], hemoglobin (Hb) and myoglobin (Mb) have been used to detect nitrite in recent years. However, as their name suggests, these proteins are not specific to nitrite and are often designed to target multiple analytes, including peroxide, oxygen, trichloroacetic acid, and BrO_3^-. The development has primarily been focused on improving substrate electrode materials and studying protein immobilization techniques.

Historically, cytochrome *c* and HRP-based biosensors were used to detect hydrogen peroxide. However, recent studies have demonstrated their potential for nitrite measurement. One such biosensor utilized the HRP enzyme encapsulated in Co_3O_4 nanosheets/RGO composite. Nitrite reduction was facilitated by binding to the redox-active Fe site of HRP, resulting in an irreversible reduction peak at −0.71 V (vs. Ag/AgCl). The authors reported good repeatability in biosensor preparation and stable sensor response for at least 4 weeks [94]. Another study explored the catalytic oxidation of nitrite to nitrate using cytochrome *c* immobilized in a composite material based on multi-walled carbon nanotubes (MWCNT) and the conducting polymer poly(3-methylthiophene). Ferrous cytochrome *c* is oxidized to the highly reactive ferric state (Fe^{4+}), which is capable of oxidizing nitrite. Detection was achieved by amperometry at +0.9 V (vs. Ag/AgCl) [95].

Biosensors based on Hb exploit its heme proteins for their redox activity. The electrocatalysis involves the reduction of nitrite to N_2O using the hemoglobin ($HbFe^{2+}$)/methemoglobin ($HbFe^{3+}$) system. This electroreduction is generally not influenced by many interferents, as discussed in section 3.1. In most studies, nitrite detection is observed around the −0.6/−0.7 V (vs Ag/AgCl) range. Hb has been immobilized in various composite materials, including graphene oxide/ionic liquid composites [96], SWCNT microbelts [97], layered Ti_3C_2-based materials [98], and ionic-liquid/TiN nanoparticles [99]. These biosensors typically exhibit good performance with sub-micromolar LODs, and their application has been tested in various matrices, such as water samples, sausage, and milk. One of the biosensors demonstrated good stability when stored at 4°C for at least 4 weeks [98]. The same functionality can also be achieved using another heme protein, myoglobin (Mb). Again, significant progress has been made in developing substrate materials, such as single-layer graphene nanoplatelet–protein composite film [100] or SWCNT [101].

2.3.3. *Biosensors based on nitrite reductases*

In the category of nitrite-reducing enzymes, two types are commonly employed in nitrite biosensing: ammonia-forming nitrite reductases and nitric oxide-forming nitrite reductases. Biosensors based on these enzymes exhibit the highest selectivity for nitrite detection of all electrochemical sensors.

The first type, a copper-containing nitrite reductase (Cu-NiR), catalyses the reduction of nitrite to nitric oxide. This reaction involves the exchange of only one electron, which negatively impacts the sensitivity of this method. In recent years, Cu-NiR has been used exclusively with a mediator, specifically a viologen-modified polysiloxane, which is co-immobilized with the enzyme. Amperometric detection achieved a LOD of 60 nM at a detection potential of −0.7 V (vs. Ag/AgCl). The biosensor demonstrated stability for a minimum of 51 days, and common interferents, such as chlorate or sulphite, did not affect nitrite determination [102].

The second type, cytochrome *c* nitrite reductase (*cc*NiR), catalyses the reduction of nitrite to ammonia, involving the exchange of six electrons, which theoretically makes these biosensors more sensitive. This enzyme was successfully entrapped in porous silica glass on a pyrolytic graphite surface, resulting in a mediator-free biosensor. The biosensor gave a response at −0.42 V (vs. Ag/AgCl), though the amperometric technique was performed at −0.9 V to achieve the best sensitivity, with an LOD of 120 nM [103]. This type of biosensor was further miniaturized using a *cc*NiR/carbon ink composite on a disposable carbon SPE. The *cc*NiR enzyme demonstrated significant resilience to various organic solvents and conditions used in carbon ink preparation. Since oxygen is a major interferent, an oxygen scavenging system based on glucose oxidase was employed to enhance the biosensor's performance in on-site applications [104]. This approach was further developed into a biosensor with a co-immobilized oxygen scavenging system (based on glucose oxidase [105] and bilirubin oxidase [20]) on a disposable carbon SPE. Nitrite was detected at around −0.5 V (vs. Ag) and was successfully applied in urine sample analysis. These resulting biosensors offer a disposable, low-cost methodology suitable for on-site applications [105].

3. Potentiometric sensors

Potentiometric sensors (Fig. 4, Table 5) are built on the measurement of a potential variation when no current is flowing through the cell. These sensors are based on the ion selective electrodes (ISE) to indicate ion activity, rather than the concentration directly. ISEs can be based on a membrane specifically designed to interact with a target ion, while separating the internal solution of the electrode and the sample solution. Another common type, solid state ISEs, have both components in a solid state. These sensors have a wide LDR with a logarithmic dependency, and they are selective to some extent (it depends on the membrane properties), but they require frequent calibration. As the dependence is logarithmic, even a small error in potential measurement can result in a high error in concentration. Therefore, the stability of the reference electrode is crucial, which, together with frequent calibration can be challenging for on-field analysis and with non-expert users [18]. Number of papers related to potentiometric sensors is approx. 20, significantly lower than sensors based on voltammetry/amperometry (see Fig. 2).

One way to enhance performance and selectivity is the development of novel membranes and ionophores. The high hydrophilicity of nitrite anion makes it hard to strongly interact with a membrane and their sensitivity is poor compared to hydrophobic anions such as ClO_4^- or SCN^-. New ionophores belonging to salophen- [106,107] and salphen- [108] type complex containing Co(III) were developed. These new ionophores have shown a response roughly in the range of 1 μM to 0.1 M with acceptable selectivity to hydrophilic anions (Cl^-, NO_3^-, Br^-, etc.). However, the problem of SCN^- interference persisted. Yang and Meyerhoff reported that Co(III) corrole ionophore could improve selectivity regarding hydrophobic anions. They also noted one important general aspect considering ISE, their lifetime, which is limited by the degradation of the membrane. In their case, two weeks were enough to drop the response significantly [109].

From a practical standpoint, the biggest challenge for nitrite ISEs with regard to their selectivity is dealing with OH^- and Cl^- anions. Chlorides are particularly problematic in seawater where their content can be as high as 600 mM. This means that even small interference is multiplied by the overwhelming content of chlorides compared to nitrites. Interferences can be avoided by some form of sample pretreatment. For example, OH^- was eliminated by in-line acidification of the sample using a cation exchanger membrane. Interference of Cl^- can be eliminated by desalination through electrolysis, where Cl^- is oxidized. This rather complex platform could detect nitrite down to 0.5 μM [110]. All-solid-state ISEs, with carbon nanotubes substituting inner ion to electron transducing layer, exhibited similar characteristics to a classical

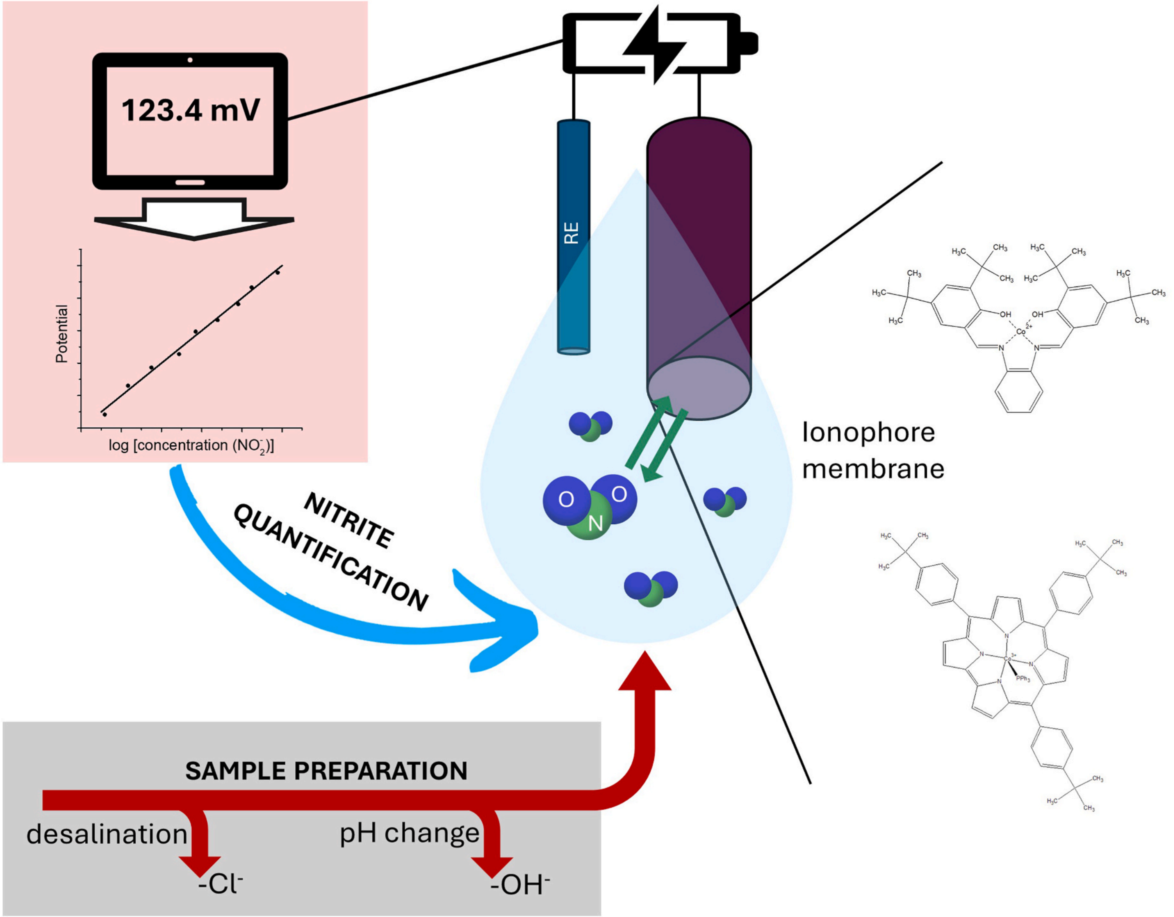

Fig. 4. Schematic of potentiometric nitrite sensors with sample preparation methods and most common structure of ionophores.

Table 5
Selected works with potentiometric sensors.

ISE ionophore	LOD, μM	LDR	Type of real sample	Selectivity, log K[a]	ref
Co(III) salophen-type	3	3 μM–1 mM	urine	Cl$^-$: −3.2, NO$_3^-$: −3.1, SCN$^-$: 0.2	[107]
Co(III) salphen-type	5.7	10 μM–0.1 M	–	Cl$^-$: −3.8, NO$_3^-$: −3.2, SCN$^-$: 0.2	[108]
Co(III) corrole	5	5 μM–0.1 M	–	Cl$^-$: −3.5, NO$_3^-$: 0, SCN$^-$: 0.5	[109]
Nitrite ionophore VI	0.38	0.38 μM–1 mM	aquarium	Cl$^-$: −3.7, NO$_3^-$: −3.3, OH$^-$: 2	[110]

[a] Log K represents the logarithm of selectivity coefficient. The value of 0 represents equal response of interferent and nitrite. For more detailed description, read [18].

liquid solution, giving an advantage mainly in the chemical and mechanical robustness and an easier manipulation. Thus developed fully automatic sensor by Cuartero et al. was implemented into a submersible probe to detect macronutrients, chloride, and pH in seawater and was successfully tested on-site in an ocean bay in France [111].

4. Conclusion

Nitrite monitoring is a crucial task for electroanalytical chemists, as demonstrated by this review. Our evaluation of the literature reveals that certain studies have significantly impacted the field, driving advancements and shaping theoretical frameworks. However, it is important to recognize that not all papers achieve the same level of impact on the topic of nitrite sensing. Some studies may have limitations that affect their broader applicability or significance in nitrite sensing but may be more influential in fields such as material research, methods for preparing complex sensing materials, or electrochemistry in general.

Sensors based on nitrite reduction have shown good applicability, as they are typically not affected by interferents other than oxygen, but this can be solved by the novel oxygen scavenging methods that were recently developed. Although there is a large number of publications on sensors based on nitrite oxidation, these sensors have struggled to surpass the performance of common metallic materials such as gold, silver, and copper (or their nanoparticles). Considering the cost, novel carbon-based materials, disposable screen-printed electrodes (SPEs), and 3D-printed carbon composites represent a promising future for nitrite sensors. However, these materials often lack selectivity due to the high oxidation potential of nitrite, and their applicability depends on the type of sample and potential interferents. Biosensors based on enzymatic nitrite reductases offer high selectivity and sensitivity, and like sensors based on reduction, they do not suffer from many interferences other than oxygen, with an acceptable shelf life. Potentiometric sensors provide good performance but are affected by interferents and have lower sensitivity.

To truly advance nitrite sensor technology, research should focus on applications in real matrices and consider the selectivity of the developed methods. The trend of creating increasingly complex electrode materials may not be the optimal path for nitrite monitoring. Additionally, factors such as ease of material construction, assembly, preparation, and cost become more challenging with the use of complex and exotic materials, noble metals, nanoparticles, and enzymes – making it difficult to apply in real-world scenarios. Another potential improvement for nitrite sensing and biosensing could involve developing low-cost and improved potentiostats, measurement software, and related technologies, as enhancing nitrite sensors does not always require improvements to the electrode material itself but may involve optimizing the entire sensing system. We believe that there is still room for improvement in these areas.

CRediT authorship contribution statement

Július Gajdár: Writing – original draft, Investigation, Data curation. **Sara Rodrigues Gaspar:** Writing – original draft, Data curation. **M. Gabriela Almeida:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

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Data availability

No data was used for the research described in the article.

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