Electrochemical detection of sulfite in food samples

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Received: October 21, 2022; Accepted: November 8, 2022; Published: November 29, 2022

Abstract

In various pharmaceutical and food industries, sulfite is utilized for the inhibition of nonenzymatic and enzymatic browning. Also, in brewing industries, it acts as an antioxidizing and antibacterial agent. Several toxic and adverse reactions, including vitamin deficiency, hypersensitivity, and allergic diseases, have been attributed to sulfite ingestion that may cause dysbiotic oral and gut microbiota events. Thus, the content of sulfite in foods must be controlled and monitored, and it is essential to find a specific, reproducible, and sensitive method to detect sulfite. Some analytical solutions are being tested to quantify sulfite. However, due to their advantage over traditional techniques, electroanalytical techniques are attracting much attention because they are simple, fast, affordable, and sensitive to implement. In addition, by the electrode modification, the morphology and size can be controlled, resulting in the miniaturization to be used in portable electrochemical devices. Therefore, the present review addressed some articles on the electrooxidation of sulfite from real samples using various electrochemical sensors.

Keywords

Sulfite; modified electrode; voltammetry; electrooxidation; amperometry

Introduction

Experts in the field have largely considered the sulfite contribution and its respective alter ego, that is, sulfur dioxide, into agri-food products due to its impact on some medical conditions. The presence of sulfite produces different technical impacts on various kinds of food products like inhibiting the enzymatic browning in fresh products and shrimp, inhibiting the nonenzymatic browning in the dried or dehydrated vegetables and fruits, anti-microbial actions in wine-making and wet-corn milling, anti-oxidant impact, bleaching in the maraschino cherries and hominy and dough conditioning [1-4]. Additionally, sulfite is utilized for preserving the effectiveness and stability...
of specific medicines. Put differently, the increased concentration of sulfite causes an allergic reaction in sensitive consumers. In general, human serum shows a sulfite concentration in ranges between 0 and 10 μM. Moreover, the US Food and Drug Administration (FDA) suggested the existence of warning labels on all food products consisting of more than 10 mg/kg sulfite or beverages consisting of >10 mg/L sulfites. For this reason, sulfite content must be cautiously controlled in foodstuffs [5-8].

Researchers have presented various methods to determine sulfite in the beverages and food like titrimation, flow injection analysis (FIA), iodimetry, ion chromatography, spectro-photometry, chemiluminescence, fluorometry, high-performance liquid chromatography (HPLC) as well as gas chromatography. Nonetheless, a number of them do not have accuracy and sensitivity (for example, spectrophotometry and iodimetry) and other methods need laborious sample preparation, costly instrument and professional experts [9-14].

Experts in the field utilized electrochemical systems as one of the solutions to the decentralized testing for numerous specimens because they required cheap equipment and inexpensive operations, could be miniaturized, and have been accessible by simple-dipstick sampling [15-35]. In addition, electrochemical methods have been considered to be very selective, quantitative, less time-consuming, and strongly sensitive, and enjoy broad dynamic ranges and fast responses. Moreover, sulfite's redox features have been defined so that it is possible to reduce or oxidize the analyte to easily modify sulfite for electrochemical determination [36-70].

Nevertheless, electrochemical analysis of the analyte has been restricted by electrode surface fouling, time, and reagent consuming process for electrode surface regeneration. Notably, while developing electroanalytical sensing systems to detect an analyte, sensing electrodes would be frequently modified with proper substances to achieve favorable outcomes in selectivity and sensitivity [71-97].

As nanoscience and nanotechnology have been developed, researchers have remarkably considered nanomaterials. Thus, they contribute importantly to cases like catalysis, micro-electronics, as well as electrochemical sensors because of the respective thermal, optical, catalytic, and electrical features [98-113]. Therefore, nanomaterials would be highly feasible in enhancing the sensors' performance due to the increased surface-to-volume ratio, higher electrical conductivity, suitable biocompatibility, particularly good catalytic abilities, and surface reaction activities [114-120].

Furthermore, electroanalytical chemistry has been developed in presenting screen-printed electrodes (SPE), modified carbon-based electrodes and other electrodes. Therefore, our review is a summary of the current achievements of distinct chemically-modified electrodes for the electrochemical sensing of sulfite. Design of the mentioned sensor-enabled researchers to improve the analytical performances of the available electroanalytical sensing systems with regard to selectivity, sensitivity, multiplexed detection capability as well as field portability.

**Electrochemical detection of sulfite**

According to the research, sensing electrodes should be used for electrochemical sensing of sulfite to pass current to an aqueous solution and create a number of measurable and beneficial electrical signals relative to the electrochemical reactions in the solution of the presence of sulfite ions. Since the electrodes can be miniaturized and easily modified, the electrochemical setup would usually be shorter, simplified and portable, resulting in their effectiveness and usefulness for sulfite determination. It is possible to modify the working electrode with various substances for the specific detection of sulfite [121-123].
The diverse carbon electrodes (from the traditional large-scale carbon-based materials (e.g., glassy carbon electrodes (GCEs), carbon paste electrodes (CPEs) and graphite) to the well-known nano-sized carbon materials (e.g., carbon nanotubes (CNTs)), the screen-printed electrodes (SPEs), gold (Au) electrodes and Pt electrodes, they have a widespread utilization in the electrochemical sensing systems. These electrodes can be modified with various materials and used for the determination of the sulfite.

Glassy carbon electrodes for sulfite detection

It is widely accepted that glassy carbon (GC) artifacts have been created by a robust controlled heating plan of a pre-modelled polymeric (phenol-formaldehyde) resin body in an inert atmosphere so that the carbonization procedure initiates at a temperature >300 °C. GC has been extensively employed in voltammetric electrodes during the last twenty years. Since they exhibit lower residual current in the ranges of close to 1 V in aqueous media as well as more extended ranges in organic solvents and aqueous micellar solution, they are usually utilized as one of the indicator electrodes. Moreover, numerous papers of the GCEs exhibited higher sensitivity of the apparent rates of redox reactions toward the electrode surface state [124-131].

A lot of modified GCEs have been made to detect sulfite from real samples (Table 1). In their study, Manusha and Senthilkumar [132] introduced a new redox mediator-based ionic liquid in order to selectively and sensitively detect sulfite. Therefore, they devised phenothiazine imidazolium ionic liquid with hexafluorophosphate counter anion (PTZ-IL), synthesized it as a molten salt, and employed it as a redox mediator in preparing the modified electrode. Then, PTZ-IL was immobilized on the multi-walled carbon nanotubes (MWCNTs) deposited GCE to fabricate the PTZ IL/MWCNT/GCE modified electrode. Figures 1A and 1B present the synthetic process of PTZ-IL formation and a schema of the electrode modification. In addition, researchers applied cyclic voltammetry (CV) to examine the electrochemical functions of the PTZ-IL/MWCNT/GCE. It has been found that this new sensor has a redox couple with the cathodic and anodic peak potentials at 0.594 and 0.707 V, which have been attributed to the phenothiazine/phenothiazine radical cation redox couple. Moreover, PTZ-IL/MWCNT/GCE exhibited very good electrocatalytic activities for sulfite oxidation, according to which an amperometric sensor has been presented to detect sulfite. Furthermore, this nonenzymatic sensor displayed a wider linear range between 30.0 and 1177.0 μM with sensitivity 282.2 μA mM⁻¹ cm⁻² and a limit of detection (LOD) equal to 9.3 μM for detecting sulfite [132].

Figure 1. (A) Synthetic process of PTZ-IL (3) and (B) schema of the construction process of PTZ-IL/MWCNT/GCE [132]
In this regard, Zhu et al. [133] addressed the synthesis of LaFeO$_3$ using the sol-gel method and thus procured the LaFeO$_3$/graphene composite materials by ultra-sonic dispersion. Then, they utilized the composite-modified electrode as the electrochemical sensor for detecting the sulfite content. According to the electrochemical test outputs, the LaFeO$_3$/graphene composite modified electrode had a suitable response signal for sulfite and the response current has been proportional to the sulfite concentration in ranges between 1.0 and 200.0 μM. Moreover, the linear relationship equaled \( I = 0.119C + 0.135 \), correlation coefficient \( (R^2) = 0.994 \), and LOD \( (S/N=3) \) equaled 0.21 μM. Finally, this new technique has been substantially utilized in the white wine samples, and the recovery rate ranged between 97.63 and 103.02 % \( (n=5) \) [133].

Moreover, Yang et al. [134] constructed a sulfite electrochemical sensor by Nafion and molybdenum disulfide (MoS$_2$). According to differential pulse voltammetry (DPV) and CV, MoS$_2$ showed very good catalytic activities for the redox of SO$_3^{2-}$. Upon the optimization of acidity of the scan rate, supporting electrolyte, and other variables for the electrochemical response of SO$_3^{2-}$, this new sensor exhibited a broad dynamic linear range between 5.0×10$^{-3}$ and 0.5 mM \( (R^2 =0.997, n=15) \) to detect SO$_3^{2-}$ with a LOD equal to 3.3 μM that may be employed for SO$_3^{2-}$ content detection in water, which enjoys benefits like acceptable reproducibility, prolonged stability, reasonable recovery and anti-interference [134].

In addition, Adeosun et al. [135] showed the electrochemical synthesis of the conductive polypyrrole chitosan (PPYCHI) thin film for sensitively detecting sulfite in real specimens. Figure 2 is a schema of this synthetic process. As seen, this co-polymeric PPY-CHI film has acceptable electrocatalytic behaviors for oxidizing sulfite. Therefore, it has been employed to detect sulfite with DPV and a LOD, linearity, and sensitivity equal to 0.21 μM \( (S/N = 3) \), 50.0 to 1100.0 μM and 15.28 μA μM cm$^{-2}$, respectively [135].

![Figure 2. Schema of the synthetic process for electro-polymerization of poly-pyrrolechitosan](image)

Furthermore, Pandi et al. [136] electrodeposited the completely organized lutetium(III) hexacyanoferrate micro-particles on the poly(taurine) modified GCE; that is, (LuHCF/poly(taurine)-GCE). It has been found that this LuHCF/poly(taurine)-GCE enjoys very good electrochemical activity as well as higher sensitivity for sulfite sensing. They also examined the electrochemical oxidation of sulfite on the LuHCF/poly(taurine)-GCE using DPV and CV. Results have shown that this modified electrode had higher sensitivity equal to 448.0 μA mM$^{-1}$ cm$^{-2}$ and 1.33 μM LOD for electrochemical oxidation of sulfite with more acceptable functionality and selectivity [136].

Moreover, Yu et al. [137] study dealt with the synthesis of Au NPs-reduced graphene oxide composite (AuNPs-rGO) using the chemical coreduction method with ethylene glycol (EG) as the reducing agent. Therefore, they modified the GCE with an AuNPs-rGO composite through the dropping method. In addition, researchers employed CV and electrochemical impedance spectroscopy (EIS) to investigate electrochemical behavior and electrocatalytic activities of the AuNPs-rGO/GCE
electrode for sulfite oxidation. With regard to the outputs, AuNPs-rGO/GCE has higher electrochemical activities to oxidize sulfite through the synergistic effect of the rGO and AuNPs. Based on the results in 0.10 M \( \text{H}_2\text{SO}_4 \), the linear range for sulfite detection via amperometry at 0.40 V versus SCE equaled 20.0 to 2300 \( \mu \text{M} \) \((R^2=0.995\, 6)\) with the LOD equal to 45 nM \((S/N = 3)\) [137].

In their study, Devadas et al. [138] reported a shape-controlled preparation of praseodymium hexacyanoferrate (PrHCF) with a simple electrochemical procedure. Therefore, the electro-chemically fabricated PrHCF-modified GCE showed very good electrocatalytic activities for sulfite oxidation. Electrochemical oxidation of sulfite on the PrHCF-modified GCE has been examined by the linear sweep voltammetry (LSV) and CV. Results have shown this sulfite sensor sensitivity equal to 0.036 mA mM\(^{-1}\) cm\(^{-2}\) and lower LOD as 2.15 mM. Finally, researchers detected sulfite from the specimens obtained from the tap water and red wine to confirm the real-time utilization of the PrHCF-modified GCE [138].

Wang and Xu [139] presented one of the new methods for selectively extracting the free (pH 8.4) and total sulfite (pH 11.0) from the muscle foods and the following detection by a voltammetric sensor. Their technique has been on the basis of electrocatalytic oxidation of sulfite at the modified GCE constructed by immobilization of 9 \( \mu \text{g} \) of acetyl-ferrocene (AFc) over the GCE surface along with 35 \( \mu \text{g} \) of carbon black (CB) for improving the electron transfer into the poly(vinyl butyral) (PVB) membrane matrix. Results indicated linearity of the external standard calibration curve in ranges between 0.03 and 4.0 mM with 15 \( \mu \text{M} \) LOD. Ultimately, this new technique could be utilized for determining free and total sulfite in the shrimp muscle-fortified specimens [139].

<table>
<thead>
<tr>
<th>Table 1. Modified GCEs to detect sulfite</th>
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<tbody>
<tr>
<td>GCE modified with</td>
</tr>
<tr>
<td>PTZ IL/MWCNT</td>
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<tr>
<td>LaFeO(_x)/graphene</td>
</tr>
<tr>
<td>MoS(_x)/-NF</td>
</tr>
<tr>
<td>PPy-CHI</td>
</tr>
<tr>
<td>LuHCF/poly(taurine)</td>
</tr>
<tr>
<td>AuNPs-rGO</td>
</tr>
<tr>
<td>PrHCF</td>
</tr>
<tr>
<td>AFc/CB/PVB</td>
</tr>
</tbody>
</table>

CPEs for sulfite detection

It is widely accepted that carbon paste, as one of the mixtures of graphite powder and an appropriate liquid binder, is the most flexible substrate for biological and chemical modifications. It is notable that the heterogeneous features of the CPEs, specific effects of the liquid binder, variability in the employed carbon material, and diverse proportional compositions need extensive and reliable characterization procedures [140-145]. Because of multiple beneficial features, CPEs have widespread utilization in electrochemical measurements. [146-152]. Table 2 tabulates information about modified CPEs, reported by various works.

In this regard, Zabihpour et al. [153] dealt with the incorporation of the MgO/SWCNTs nanocomposite and 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [Bmim][Tf2N] into the CP matrix for obtaining a modified CPE (MgO/SWCNTs-[Bmim][Tf2N]-CPE) as the electroanalytical instrument. According to the results, MgO/SWCNTs-[Bmim][Tf2N]-CPE created a better analytical oxidation signal for ferulic acid (FA) that was 3.17 times higher than the un-modified sensors. Moreover, this electrode produced distinctive electrooxidation signals for FA with \( \Delta E_p=300 \text{ mV} \) in the
presence of sulfite, verifying its utility for FA detection in the presence of sulfite ions that are usually found in the food samples such as red wine. Additionally, MgO/SWCNTs-[Bmim][Tf2N]-CPE has been shown as one of the robust tools for FA and sulfite ions detection with the recovery data of 97.84 to 103.1 % in the concentration range between 0.009 and 450.0 μM as well as 0.1 and 450.0 μM with a LOD equal to 3.0 nM and 50.0 nM [153].

In addition, Norouzi and Parsa created a modified electrode in the course of the electropolymerization of 4-aminobenzoic acid in the presence of sodium dodecyl sulfate (SDS) [154]. Therefore, they incorporated the Ni(II) ions into the polymer by immersing the modified electrode into a 0.1 M Ni(II) ions solution. Then, researchers employed CV to investigate the electrochemical behaviors of the Ni/poly(4 amino benzoic acid)/sodium dodecyl sulfate/CPE (Ni/poly(4-AB)/SDS/CPE). Results have shown the acceptable activities of the polymer-modified electrode for sulfite electrooxidation in a phosphate buffer solution (PBS) at a pH of 11, and finally, LOD equaled 0.063 mM. Based on the optimum experimental condition, the peak current response linearly enhanced as the sulfite concentration elevated in ranges between 0.1 - 1.0 and 1.0 - 10.0 mM [154].

Furthermore, Miraki et al. [155] presented one of the electrochemical platforms based on the CPE modified with the NiO NPs and acetyl-ferrocene (AF) (CPE/NiO-NPs/AF). According to the findings, CPE/NiO-NPs/AF had acceptable electrocatalytic activities to detect sulfite in the concentration range of 0.005 to 500.0 μM with a LOD of 0.001 μM. It has been found that the electrocatalytic interactions of sulfite with AF at the CPE/NiO-NPs/AF surface may resolve the overlapping single of nitrite and sulfite for their simultaneous detection. Finally, researchers found a higher performance of CPE/NiO-NPs/AF to detect nitrite and sulfite in wastewater samples [155].

In another study by Winiarski et al. [156] water-soluble form of 3-propyl(4-methyl-pyridinium) silsesquioxane chloride (Si4Pic‘Cl) has been synthesized and characterized. Therefore, researchers demonstrated its potency to be utilized as one of the stabilizing agents for AuNP. In fact, CPEs modified with the Si4Pic‘Cl and AuNP has been fabricated and employed in detecting and quantifying sulfite in the acidic medium. With regard to the voltammetric signal for sulfite, the electrode modified with the AuNPs (CPE/Au-Si4Pic‘Cl) exhibited an electrocatalytic impact of ca. -0.20 V in comparison with the bare electrode. According to the square wave voltammetry analysis (SWVA) and based on the optimum experimental condition, the reduction peak enhanced as the sulfite concentration elevated in ranges between 2.54 and 48.6 mg L⁻¹. Finally, LOQ and LOD equaled 2.68 and 0.88 mg L⁻¹ for sulfite [156].

Another study conducted by Sroysee et al. [157] described an amperometric sulfite bio-sensor, which contained a CPE (Fe3O4@Au- Cys-FA/CPE) modified with the immobilized sulfite oxidase (SOx) on an Au-coated magnetite NP core encased within a conjugated folic acid (FA) cysteine (Cys) shell. Therefore, a poly-dimethylsiloxane (PDMS), as well as a mineral oil mixture as the binder, was used to manufacture the bio-sensor electrode, which enhanced the sensitivity and physical stability of the electrode. Figure 3 is an illustration of the preparation process of the sulfite bio-sensor. The Fe3O4@Au-Cys-FA electrode exhibited acceptable electrocatalytic activities with reasonable retention of the chemisorbed SOx on the electrode due to the respective larger surface areas. Then, researchers employed amperometric measurements from the Fe3O4@Au Cys-FA/CPE biosensor to quantify sulfite and used an in-house assembled flow cell at +0.35 V (versus Ag/AgCl) with the PB carrier of 0.10 M at a pH of 7.0 and the flow rate equal to 0.8 mL min⁻¹. Ultimately, this system detected sulfite between 0.1 and 200.0 mg L⁻¹ with 10 mg L⁻¹ LOD (3 s of blank) [157].
It is notable that Silva et al. [158] also devised a square-wave voltammetric technique with regard to the sulfite electrochemical reduction to quantify this preservative in commercial beverages. Therefore, they used CPE chemically modified with the MWCNTs as the working electrode. It was found that at the optimal experimental condition, the linear response to the sulfite concentration ranges between 1.6.0 and 32.0 mg SO$_2$ L$^{-1}$ (25.0 to 500.0 µM of sulfite) and LOD equals 1.0 mg SO$_2$ L$^{-1}$ (16 µM of sulfite) [158].

**Table 2. Modified CPEs to detect sulfite**

<table>
<thead>
<tr>
<th>CPE modified with</th>
<th>Method</th>
<th>LOD</th>
<th>Linear ranges</th>
<th>Real samples</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO/SWCNTs-[Bmim][Tf2N]</td>
<td>DPV</td>
<td>50.0 nM</td>
<td>0.1-450.0 µM</td>
<td>Red wine, white rice</td>
<td>[153]</td>
</tr>
<tr>
<td>Ni/poly(4-AB)/SDS</td>
<td>Amperometric</td>
<td>0.063 mM</td>
<td>0.1 - 10.0 mM</td>
<td>Weak liquor</td>
<td>[154]</td>
</tr>
<tr>
<td>NiO-NPs/AF</td>
<td>DPV</td>
<td>0.001 µM</td>
<td>0.005 - 500.0 µM</td>
<td>Wastewater</td>
<td>[155]</td>
</tr>
<tr>
<td>Au-Si4Pic+Cl</td>
<td>SWV</td>
<td>0.88 mg L$^{-1}$</td>
<td>2.54 - 48.6 mg L$^{-1}$</td>
<td>White wine A, white wine B and coconut water</td>
<td>[156]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$@Au Cys-FA</td>
<td>Amperometric</td>
<td>10 mg L$^{-1}$</td>
<td>0.1 – 200 mg L$^{-1}$</td>
<td>-</td>
<td>[157]</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>SWV</td>
<td>16 µM</td>
<td>25.0 - 500.0 µM</td>
<td>Coconut water, fruit juices and white wine</td>
<td>[158]</td>
</tr>
</tbody>
</table>

**SPEs for sulfite detection**

Screen-printed technology involves the layer-by-layer deposition of ink on a solid substrate by a screen or mesh, which defines the sensor geometry. Such a new technology enjoys design flexibility, acceptable reproducibility, process automation, and a selection of diverse substances. However, SPEs do not possess problems encountered with the classical solid electrodes, like laborious cleaning procedures and memory effects. Finally, analyses have provided a new window due to the broad ranges of the form of the SPEs modification [159-181]. Table 3 tabulates information about modified SPEs, which have been reported by various works.

Aflatoonian et al. [182] reported synthesizing the MOWS$_2$ nano-composite and employed DPV, CV, and chrono-amperometry (CHA) to examine the electrochemical behaviours of sulfite on the
SPEs modified with MOWS$_2$ nano-composite. According to the electrochemical specification, researchers observed acceptable electrocatalytic activity and surface area impact of the MOWS$_2$ nano-composite. They also found a considerable enhancement of oxidation signals of sulfite on the MOWS$_2$/SPE compared to the bare SPEs. Ultimately, with regard to the optimal condition, sulfite quantification ranged from 0.08-700.0 μM with a lower LOD of 0.02 μM ($S/N=3$) \[182\].

Furthermore, Hemmati et al. [183] dealt with synthesizing the Fe$_3$O$_4$ NPs via a solvothermal approach using ethylene glycol (EG). Then, the dropping procedure was used to modify the GSE with the Fe$_3$O$_4$ NPs. Researchers also employed DPV, CHA, and CV for investigating electrocatalytic activities as well as the electrochemical behavior of Fe$_3$O$_4$/SPE electrodes for sulfite oxidation. According to the DPV analysis and based on the optimal experimental condition, the oxidation peak enhanced as the sulfite concentration elevates in ranges between 0.5 and 100.0 μM. Finally, LOD equaled 0.1 μM for sulfite [183].

Moreover, Maaref et al. [184] designed their electrochemical technique to detect sulfite using Schiff-base modified graphite SPEs as a disposable chemo-sensor. Therefore, they used differential pulse voltammmograms of the modified SPE in the presence of sulfite and observed a typical peak current at 350 mV. Moreover, they found the linear sensor responses in the concentration ranges between 0.5 and 300.0 μM of the analyte. Finally, LOD equaled 0.3 μM for sulfite, and thus, this method could be used for sulfite detection in natural water samples [184].

In their study, Molinero-Abad et al. [185] modified the screen-printed carbon electrodes (SPCEs) with tetrathiafulvalene (TTF) and sulfite oxidase enzyme in order to selectively and sensitively detect sulfite. Therefore, they optimized the amperometric experimental condition regarding the significance of the sulfite quantification in the wine samples and the innate complicatedness of the samples, specifically red wine. Researchers observed the biosensor response to sulfite with a cathodic current (at 200 mV versus the SP Ag/AgCl electrode and pH 6) in the broad concentration ranges with 6.0 μM LOD at 60 °C. Therefore, this method could be employed for sulfite detection in red and white samples, with the average recovery equal to 101.8 and 101.5 % [185].

Consequently, Molinero-Abad et al. [186] reported an amperometric detection of sulfite with the use of the SPCEs modified with Au NPs. It has been found that the electrode is relatively selective and shows responses to sulfite with the oxidation current at 300 mV and pH of 6 in the concentration ranges between 9.80 and 83.33 μM, with the recoveries in ranges between 96 and 104 %. Hence, this method could be employed for sulfite detection in pickle juice, vinegar, and drinking [186].

### Table 3. Modified SPEs to detect sulfite

<table>
<thead>
<tr>
<th>SPE modified with</th>
<th>Method</th>
<th>LOD, μM</th>
<th>Linear ranges, μM</th>
<th>Real samples</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOWS$_2$</td>
<td>DPV</td>
<td>0.02</td>
<td>0.08 - 700.0</td>
<td>River and well water</td>
<td>[182]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>DPV</td>
<td>0.10</td>
<td>0.5 - 100.0</td>
<td>Water samples</td>
<td>[183]</td>
</tr>
<tr>
<td>Schiff-base</td>
<td>DPV</td>
<td>0.30</td>
<td>0.5 - 300.0</td>
<td>Well and river water</td>
<td>[184]</td>
</tr>
<tr>
<td>Tetra-thiаfulvalene and sulfite oxidase enzyme</td>
<td>Amperometric</td>
<td>6.00</td>
<td>9.9 - 82.6</td>
<td>White and red wine</td>
<td>[185]</td>
</tr>
<tr>
<td>Au NPs</td>
<td>Amperometric</td>
<td>9.80</td>
<td>9.80 - 83.33</td>
<td>Pickle juice, vinegar and drinking water</td>
<td>[186]</td>
</tr>
</tbody>
</table>

**Other kinds of sensors for sulfite detection**

A composite has been prepared by Do Carmo et al. [187] from titanium (IV) silsesquioxane and phosphoric acid (TTiP) and then occluded into HFAU zeolite (ZTTiP). In the next step, the material was modified chemically with nickel and potassium hexacyanoferrate(III) (ZTTiP NiH). Afterward, a...
modified GPE was used to obtain the voltammetric behavior of ZTTipNiH, which indicated a completely organized redox couple with KCl (3 M) (20 wt.%; \( v = 20 \text{ mV s}^{-1} \); KCl; 1.00 M) and a formal potential of \( E_{a}^{\circ}=0.51 \text{ V} \) (versus Ag/AgCl (sat.)) that corresponded to the Ni\(^{II}\)Fe\(^{III}\)(CN)\(_6\)/Ni\(^{II}\)Fe\(^{III}\)(CN)\(_6\) redox process. Upon the precise voltammetric examinations, the GPE modified with ZTTipNiH has been employed for easy and fast determination of sulfite. Then, according to the analytical curve, a linear response has been achieved in the concentration range between 0.05 and 0.80 mM, the LOD (3\( \sigma \)) equal to 0.05 mM, amperometric sensitivity equal to 14.42 mA M\(^{-1}\) and the relative standard deviation (RSD) equal to 4.21 % (\( n = 3 \)) for sulfite [187].

In addition, Preecharueangrit et al. [188] made their amperometric sulfite sensor on the basis of the nickel hexacyanoferrate (NiHCF) electrodeposited on a layer of the ordered mesoporous carbon, which has been covered on an Au electrode surface (NiHCF/OMC/Au). This NiHCF/OMC/Au had acceptable electrocatalytic activities for sulfite oxidation, and at the optimized condition, their sensor linearly responded in the concentration ranges between 2.5 \( \mu \)M to 50 mM and a 2.5 \( \mu \)M LOD (with the \( S/N \) ratio equal to 3). Finally, the electrode showed higher operational stability so that it could be applied up to 104 times (with an RSD equal to 5.9 %) and acceptable electrode-to-electrode repeatability (with an RSD of less than 7.0 %, for \( n = 6 \)) [188].

Furthermore, Devaramani et al. [189] presented one of the simplified strategies for covalent anchoring of the cobalt hexacyanoferrate (CoHCF) particles on the graphitic carbon substrate with the use of p-phenylenediamine as the linker molecule. Therefore, they made a pellet electrode by the CoHCF particles modified graphitic carbon and employed it in the electrocatalytic oxidation of sulfite. Their sensor exhibited a linear range of concentration of 4.0 to 128.0 \( \mu \)M of sulfite with a limit of quantification (LOQ) of 5.8 \( \mu \)M and 1.7 \( \mu \)M LOD [189].

Moreover, Adeloju and Hussain [190] addressed the modification of a platinum electrode surface with platinum NPs (PtNPs). Therefore, they entrapped the enzyme sulfite oxidase (SO\(_x\)) on the respective surface in an ultra-thin poly-pyrrole (PPy) film, and thus, those PtNPs with 30 to 40 nm diameter have been deposited on the Pt electrode (PtNPs/PPy-SO\(_x\)/Pt electrode) via cycling the electrode potential 20 times from -200 to 200 mV at the sweep rate equal to 50 mV s\(^{-1}\). Additionally, researchers used CV, EIS, potentiometry, and chrono-potentiometry to examine the electrochemical behaviors of the PtNPs/PPy-SO\(_x\) film. Based on the optimal condition, this biosensor showed 57.5 mV decade\(^{-1}\) sensitivity, a linear response between 0.75 and 65 \( \mu \)M of sulfite, 12.4 nM LOD, and a response time between 3 and 5 s [190].

In another study, Rawal and Pundir [191] immobilized the sulfite oxidase (SO\(_x\)) (EC 1.8.3.1) purified from Syzygium cumini leaves over the Prussian blue NPs/poly-pyrrole (PBNPs/PPY) nanocomposite film that was electrodeposited on the Au electrode surface. Therefore, they built their electrochemical sulfite bio-sensor with the use of a SO\(_x\)/PBNPs/PPY/Au electrode as the working electrode, Pt wire as the auxiliary electrode linked by a potentiostat as well as Ag/AgCl as the standard electrode. Their bio-sensor has shown optimal response within two seconds while working at 20 mV s\(^{-1}\) in 0.1 M Tris - HCl buffer at a pH of 8.0 and a temperature of 30 °C. Researchers showed the minimum LOD and linear range to be 0.1 \( \mu \)M (\( S/N=3 \)) and 0.5-1000.0 \( \mu \)M. This sensor has been assessed with 95.0 % recovery of the added sulfite in the samples of red wine and 1.9 and 3.3 % within and between the batch coefficients of variations [191]. Table 4 tabulates information about other kinds of sensors, which have been reported by various works.
### Table 4. Other kinds of sensors to detect sulfite

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Method</th>
<th>LOD, μM</th>
<th>Linear ranges, μM</th>
<th>Real samples</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZTTiPNiH/GPE</td>
<td>CV</td>
<td>50</td>
<td>50 - 800</td>
<td>-</td>
<td>[187]</td>
</tr>
<tr>
<td>NiHCF/OMC/Au electrode</td>
<td>Amperometric</td>
<td>25</td>
<td>2.5 - 5000</td>
<td>Instant noodles, noodles and macaroni</td>
<td>[188]</td>
</tr>
<tr>
<td>CoHCF particles /graphitic carbon electrode</td>
<td>Amperometric</td>
<td>1.7</td>
<td>4.0 - 128.0</td>
<td>Tomato ketchup, wine, jam, sugar and dry grapes</td>
<td>[189]</td>
</tr>
<tr>
<td>PtNPs/PPy-Sox/Pt electrode</td>
<td>Potential - time</td>
<td>0.0124</td>
<td>0.75 - 65.5</td>
<td>Wine and beer</td>
<td>[190]</td>
</tr>
<tr>
<td>SOx/PBNPs/PPY/Au electrode</td>
<td>EIS</td>
<td>0.1</td>
<td>0.5 - 1000.0</td>
<td>Red, rose and white wine</td>
<td>[191]</td>
</tr>
</tbody>
</table>

### Conclusions

Researchers have provided diverse electrochemical sensors to detect sulfite in different specimens due to the necessity of the application of a rapid procedure for determining the content of sulfite in food samples. Moreover, modifying the electrochemical sensors referred to the enhanced current responses for sulfite electrooxidation, anti-fouling impact, and higher selectivity, stability, and sensitivity. In general, we overviewed 3 types of electrochemical sensors, including the modified GCEs, the modified CPEs, and the modified SPEs. Since GCEs were proposed to be the most applied substrates for modifications, they have larger diameters, whereas the SPEs and CPEs are miniaturized instruments with very few samples. In fact, CPEs are inexpensive and can be easily prepared. In addition, they exhibited rapid regeneration of the active surface areas with the ability to eliminate the fouling effects. While preparing the CPEs, an oily binder would be employed to create the paste, and this mineral oil has been considered one of the insulating materials and a reason for lower current ranges while utilizing SPE or GCE. In this way, the problem has been resolved and the use of ionic liquids as the binder materials for CPE formation has shown that ILs have higher viscosity and conductivity. Therefore, the kind of real specimens employed should influence choosing the electrochemical sensor to detect sulfite. A number of utilizations require lower LOD; others demand wider concentration ranges, and a number of them should use strongly stable and selective methods, whereas others should entail concentration ranges greater than micro-molar sulfite levels. We hope to provide a bridge to connect the gap between food and environmental science and nanotechnology. Thus with collaborative endeavors of scientists/engineers in both fields, more novel nanomaterials-based sensors will be designed, and new solutions will spring up.

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