Electroanalytical methods for the determination of sulfite in food and beverages

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The detection of sulfite has long held the interest of the analytical community because of the large number or roles that the anion can play within environmental and physiological systems. However, the need to monitor the anion in food and drinks has risen to considerable prominence in recent years, because concerns over its ability to aggravate asthmatic conditions have increased. More restrictive legislative instruments are now being introduced to inform consumers of sulfite content, so small producers must now declare the concentration of the preservative in food produce.

This article provides a brief overview of the chemistry that underpins the preservative role and action of sulfite and aims to provide a critical assessment of the latest developments in electrochemical monitoring technologies. The main remit is not to describe the intricacies of laboratory-based techniques but rather to focus on the potential transferability of the underlying technologies to formats that could be of use for commercial food producers for decentralised testing.

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1. Introduction

The role of sulfite and its alter ego, sulfur dioxide, within agri-food produce has come under close scrutiny in recent years as concerns over its influence on a number of medical conditions have increased [1,2]. Sulfite is widely used as a broad-spectrum preservative (E220–228) to prevent microbial spoiling and browning reactions across a wide range of consumable products [3–8]. Legislative instruments have been imposed in many countries and, while not restricting its use, typically require more elaborate labelling on the packaging where concentrations exceed 10 ppm. There is a clear need to facilitate the monitoring of sulfite levels in food and drink processing to ensure the efficient utilisation of the agent in its various guises but, also to maintain compliance with the appropriate regulatory guidelines.

However, the determination of sulfite is fraught with a number of difficulties, irrespective of the analytical methodology employed. Achieving the required selectivity and sensitivity for low-level detection in a complex matrix through the use of classical titration requires considerable skill – procedural and interpretative – on the part of the analyst to ensure accuracy [9–13]. Routine analysis, as increasingly demanded by food-standard authorities, will require implementation of instrumental techniques capable of high-throughput analysis. It is unlikely that a small-scale food producer will possess the necessary chemical expertise or have the investment capacity for the purchase, operation and maintenance of such systems.

Electrochemical systems have long been proffered as a solution to decentralised testing for many species, given the low cost of the instrumentation, the promise of user accessibility through simple dipstick sampling and the potentially favourable economics of their operation [14]. This is evidenced by the disposable screen-print systems routinely used by diabetics for home-glucose monitoring [15,16]. The redox properties of sulfite are such that the analyte can be reduced or oxidised [9] so sulfite should be readily amenable to electrochemical detection.

While there are a number of colorimetric sampling systems, there are no commercial electrochemical sensors for sulfite – in any form. The aim of this review was to uncover the reasons for the absence of

such systems and highlight the progress being made towards their realisation. The remit of our investigation was limited to analysis of the analyte within biological matrices, particularly those of direct relevance to the food and drink industries. However, the content will have clear resonance with the application of electro-chemical sensing to environmental monitoring where sulfur dioxide is a prime protagonist in air pollution.

There have been many developments in the measurement of sulfite – many of which are incremental. This review does not seek to provide a comprehensive critique on the merits of each but, rather, seeks to provide an overview of the different methodologies that have been developed and that are currently being used, and to highlight their advantages and limitations. This is mainly within the remit of trying to assess critically which technologies may ultimately benefit small-scale food producers with little access to, or resources for, conventional laboratory-scale analytical instrumentation.

2. Preservative action of sulfite

The main interest in sulfite lies in its reducing properties. These are well established and play an important part, along with ascorbate, in the anti-oxidant defence that minimises the degradation of food and drink that would otherwise occur were the products left exposed to air [3–8].

Sulfites, in their various guises, can be found in: processed meats; wines, beer and cider; soft drinks and fruit juices; jams and jellies; dried, tinned and pickled fruits; shell fish; and, processed food products where the rancidity of fats needs to be prevented. The concentration of sulfite can vary considerably from one product to another, as highlighted in Table 1, and will depend on the nature of the product and the subsequent processing [17–21]. The role of the preservative in most pre-packaged fruit and vegetable produce (particularly those that have been cut or sliced) and shellfish is largely to increase shelf life through preventing the browning reactions that lead to the discolouration of the produce and that can have a negative impact on consumer perceptions [3–8,21].

Polyphenol oxidase (PPO) is the chief enzymatic protagonist that contributes to browning and spoilage [7,8] and the enzyme action is summarised briefly in Fig. 1. The oxygen-mediated conversion of phenolic derivatives (I) to the highly reactive *o*-quinone (II) intermediates promotes a cascade of reactions leading to the formation of the undesirable coloured products. Sulfite has a dual action in that it acts directly to inhibit the enzyme but also reduces the *o*-quinone to the more stable 1,2-dihydroxybenzene (III), thereby terminating the browning reaction at an early stage. The ability of sulfite to prevent the further oxidation of polyphenolics, whether through enzymatic or chemical means, is especially important in wine production, where these components are often considered to be a significant contributor to the taste, texture and colour attributes of the final product [22,23]. They are also purported to provide a protective action in cardiovascular physiology [24,25].

The nucleophilic capabilities of the sulfite anion also play a role in maintaining food quality through the inhibition of non-enzyme, Maillard-type browning

Table 1. Concentration of sulfite in products			
Liquid samples	**No.**	**SO_3^2 (mg/L)**	**Ref.**
White wines	9	17.5	[17]
	8	52.5	[18]
	2	110	[19]
Sweet white wine	1	44	[17]
Sparkling white wine	2	21	[17]
Red wine	2	16	[17]
	4	24	[18]
	2	66	[19]
Cider	1	29	[17]
Beer	1	8	[17]
Sparkling orange juice	2	25	[17]
Still orange juice	2	210	[17]
Solid samples		**SO_3^2 (mg/kg)**	**Ref.**
Raisin		280	[20]
Apricot		1360	[20]
Apple		750	[21]
Bamboo shoots		2100	[21]
Ginger		1900	[21]
Sweet coconut		375	[21]
Sun-dried tomatoes		800	[21]
Shrimp		600	[21]

Figure 1. Enzymatic browning reaction scheme.

Figure 2. Reaction schemes highlighting the onset of non-enzymatic (Maillard) browning and the preservative action of sulfite.
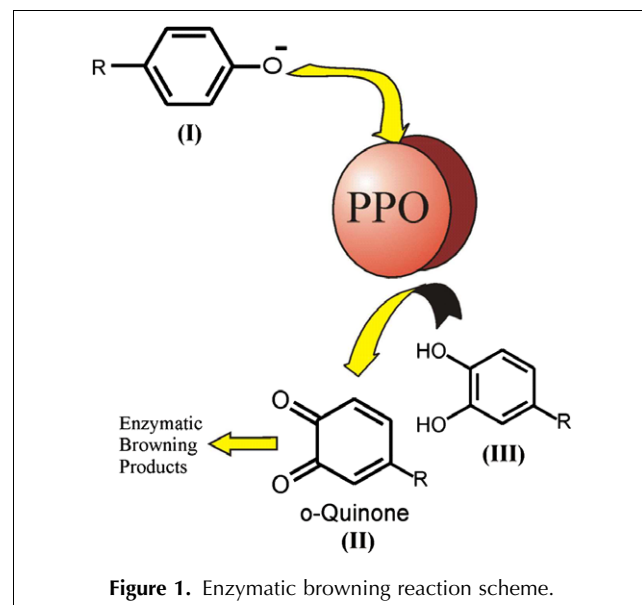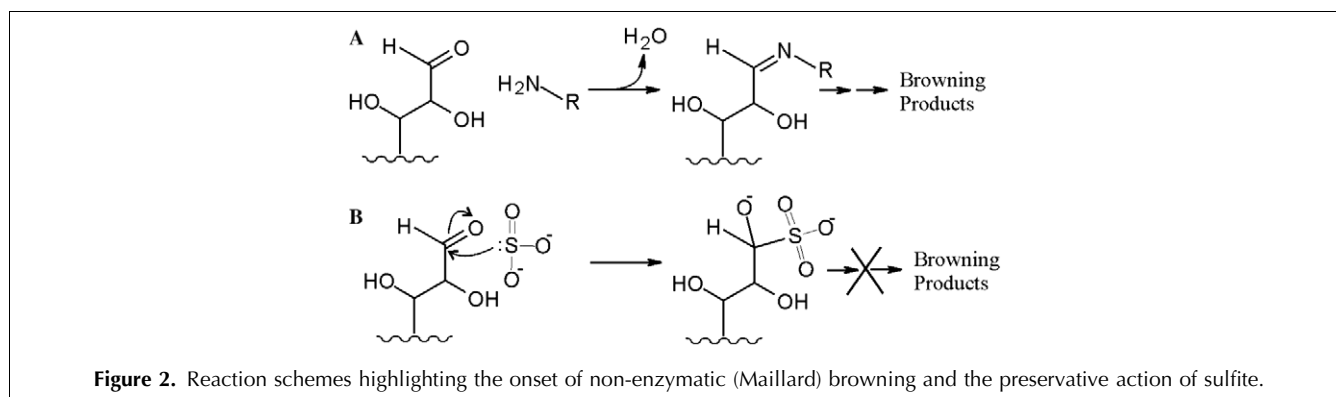
reactions [3–8]. The condensation of amine functional groups (from free amino acids or protein) with the aldehyde of reducing sugars leads to the corresponding N-substituted glycosylamine, as indicated in Fig. 2A. These intermediates can then undergo a variety of rearrangements and degradations that ultimately result in the nitrogenous polymers that provide the characteristic brown colour [3–8]. In some instances, these effects are highly valued, as they can impart favourable taste and aroma characteristics to the product – particularly baked produce. In other cases, especially with raw vegetables or meat, such by-products produce the bitter sensory characteristics associated with spoilage.

Sulfite additives add to carbonyl functionalities (Fig. 2A), effectively removing the sites at which amines can attack and thereby inhibit the non-enzymatic browning at source. The sulfite anion is a sufficiently powerful nucleophile that the reaction proceeds without the need for any acid or base catalysis [26], and it must be recognised that sulfite will be present in both free and bound forms. The reaction of sulfite with disulfide bonds (R-S-S-R) provides another route through which the chemical removal of the anion occurs [27]. The process results in the cleavage of the disulfide to yield free sulfhydryl thiol (RSH) and the corresponding sulfonic acid (RSSO$_3^-$) [27]. Such processes are widely exploited in bread products, where the sulfite-induced cleavage of the disulfide can condition (effectively weaken) the dough prior to baking [21].

3. Clinical significance

The potentially adverse health effects of sulphur-dioxide inhalation are well established, and numerous studies have investigated the association of air pollution with occupational and environmental lung diseases [28–32]. Sulfur dioxide has been shown to lead to an inflammation of the airways as a consequence of neutrophil activation and is directly implicated in the bronchoconstriction and general aggravation of asthmatic conditions [2,33]. It is through the public concerns about the latter that labelling requirements relating to the inclusion of sulfite within food and drink products have been tightened. However, recent investigations designed to assess the susceptibility of asthmatics to sulfites within wine have failed to elucidate the molecular trigger directly responsible for the asthmatic response to sulfite [2].

While the precise mechanism through which sulfite acts remains contentious, there is a body of evidence that links its presence with neutrophil activation – characterised by the sulfite-induced release of reactive oxygen species (principally H$_2$O$_2$) and chemotactic factor (IL-8) [34,35]. Neutrophils from human and animal sources have also been shown to produce sulfite spontaneously in response to stimulation from bacterial endotoxins and that points towards an ability to participate in the mediation of antimicrobial and pro-inflammatory reactions [36].

Far from being a simple exogenous additive to processed food, sulfite can arise from a variety of endogenous sources – mainly through the natural metabolic cycling of sulphur-containing amino acids. Mammalian tissues possess sulfite oxidase enzymes that convert sulfite to the less toxic sulfate and tightly regulate the systemic sulfite concentration [37,38]. The normal plasma concentration in healthy adults depends heavily on diet and lifestyle factors, and can range from 0.1 µM to 10 µM. In one study, a group of volunteers possessed basal plasma sulfite in the range 0.4–1.2 µM, and were found to have almost a 10-fold increase 1 hour after the consumption of red wine (200 mL containing 320 mg of sulfite) [38].

However, ingestion of excessive amounts of sulfite can increase the concentration to over 100 µM, but the body will normally act rapidly to counter such rises [38]. While it has been found that elevated sulfite concentrations are sustained in patients suffering from renal complications, it is unclear as to whether such increases lead to further complications or are simply a result of reduced clearance. The transient increase in sulfite through massive oral intake did not lead to any significant adverse reactions.

A recent study investigating the in vitro and in vivo nature of oral sulfite supplementation has shown that the anion can prevent lipid per-oxidation and, rather than being simply perceived as the villain of the story, could actually have a beneficial action against oxidative stress processes [39].

4. Sulfite measurement

The Association of Analytical Chemists (AOAC) has long held a standard reference method for sulfite measurement, derived from studies by Monier and Williams, and it involves a combination of distillation and end-point titration [10]. There have been numerous refinements over the years to adapt the basic methodology to particular applications, but it still retains a common core. In general, the sample is refluxed in acid (i.e. 0.5 M HCl) to liberate sulfur dioxide (Equation (1)). This is typically done under nitrogen flow with the carrier gas bubbled through a 3%-peroxide solution. The oxidation of the sulphur-dioxide gas to sulfate yields an acidic solution (Equation (2)) that is subsequently titrated with standardised hydroxide and the initial concentration of sulfite estimated.

$$SO_3^{2-} + 2H^+ \rightleftharpoons SO_2 \uparrow + H_2O \qquad (1)$$
$$SO_2 + H_2O_2 \rightarrow SO_4^{2-} + 2H^+ \qquad (2)$$
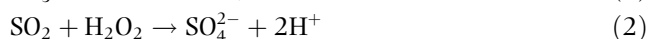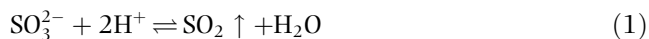
The procedure has the advantage of low capital cost, requiring little more than standard glassware and commercial reagents. However, the distillation can often be rate determining and, as such, it is far from suitable for routine analysis and is not readily applicable to the determination of low sulfite concentrations. The basic procedure is prone to false positives, whereby the transfer of volatile acids under the reflux conditions can lower the pH in the receiving flask with the subsequent acid-base titration leading to an over estimation of sulfite content [11–13]. Several modifications have attempted to counter such deficiencies and have focussed on improving the selectivity of the detection process rather than the initial separation. Iodometric titrations rely upon the direct redox interaction with the liberated sulfite/sulfur dioxide and are largely insensitive to the acidic components carried over from the distillation process [9,40]. Instrumental processes have also been coupled with ion exchange [12,13,41] and capillary electrophoretic [42] quantification of the sulfate by-product (Equation (2)), again effectively removing the interference from acidic components but with a substantial cost overhead.

Electrochemical detection has also been employed; the liberated sulfur dioxide can be directly quantified using differential pulse polarography [43], coulometry [40,44] or amperometry [12]. The last of these approaches was also assessed as a post-column detection system in ion-chromatographic systems. This is widely recognised as a more effective approach for routine sulfite determination, allowing direct quantification of liquids – minimising sample preparation and largely obviating the need for the time-consuming distillation process [12,13,17,19,45–47]. This is deemed to be more sensitive than the titration – through the combination of chromatographic resolution of components and the simplicity (and potential clarity) of the signal obtained from the electrode assembly.
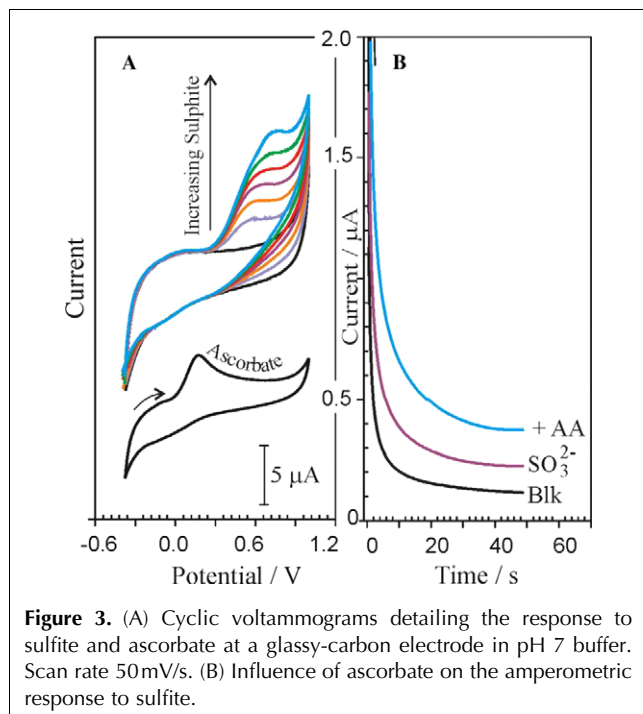
While there are several liquid chromatographic (LC) techniques for the determination of sulfite [12,13, 17,19,45–47], flow injection analysis (FIA) has tended to predominate in recent years [17,19,48–59]. Rather than relying upon column separation, the simpler FIA systems exploit the fundamental chemical properties of sulfite to enable resolution between it and other interferences. Dual-channel systems employing gas-diffusion cells or membranes (based around silicone or PTFE) are commonly used to separate the sulfite from the initial sample stream [17,48–53]. The acidification of the latter generates sulfur dioxide (as per Equation (1)), which permeates through the polymer film into the accompanying stream, where it can then be quantified using either amperometric [17,48–56] or potentiometric [57–59] detection systems.

All of these approaches require elaborate technical specification and user expertise and, as such, can incur substantial running costs. The main question now is whether the detection methodology can be simplified such that the direct determination of the analyte can be achieved with similar selectivity and sensitivity but without the complexity and cost overheads of the flow systems.

5. Direct amperometric/voltammetric methodologies

The oxidation of sulfite is usually the prime method of electrochemical detection and has been studied at a range of electrodes, including platinum [48,60], gold [61], various forms of carbon [46,62] and metal oxide [49,63]. Cyclic voltammograms detailing the oxidation of increasing sulfite (66–320 μM, pH 7) at a glassy-carbon electrode are shown in Fig. 3A and correspond to the irreversible 2e conversion to sulfate. A well-defined and quantifiable oxidation process can be obtained at most electrodes and provides an instrumentally simple route through which amperometric detectors (as advocated by the AOAC) can be constructed for the LC/FIA determination of the anion. The detection limits achievable at bare, unmodified electrodes, irrespective of substrate material, tend to be in the low micro-molar range, which is normally sufficient for monitoring both

Figure 3. (A) Cyclic voltammograms detailing the response to sulfite and ascorbate at a glassy-carbon electrode in pH 7 buffer. Scan rate 50 mV/s. (B) Influence of ascorbate on the amperometric response to sulfite.

Figure 4. Linear sweep voltammograms detailing the response to sulfite at a platinum electrode (in pH 7 buffer) under the influence of an ultrasound field. Inset: Schematic representation of the ''sono-trode'' configuration.

endogenous and exogenous sulfite. The sensitivity and the potential for integrating the detector with LC and FIA autosampler systems has, in many cases, displaced titration as the standard method.

One of the problems associated with such processes is the potential fouling of the electrode, which leads to a cumulative loss in sensitivity and compromises the reproducibility of the method [45,47]. This can be as a consequence of either sample components or the products of the oxidation process itself adsorbing onto the electrode. Pulsed amperometric detection (PAD) has been employed in an effort to minimise the loss in sensor performance through imposing multi-step waveforms that serve to clean the electrode in situ [45,47]. A more radical approach has been the development of sono-electrochemical detectors [64]. Initially developed for heavy metal analysis [65,66], they can also be used for the stand-alone (probe) detection of organics [67] and inorganic anions [68,69]. Fig. 4 highlights the components of the system along with typical voltammograms detailing the oxidation of sulfite under normal and hydrodynamic conditions, the rationale being that cavitation maintains an active surface with acoustic streaming significantly enhancing the mass transport and the sensitivity of the device [64]. The anti-fouling capabilities of such devices have been proved in a variety of food matrices ranging from wine [65] to egg homogenate [68].
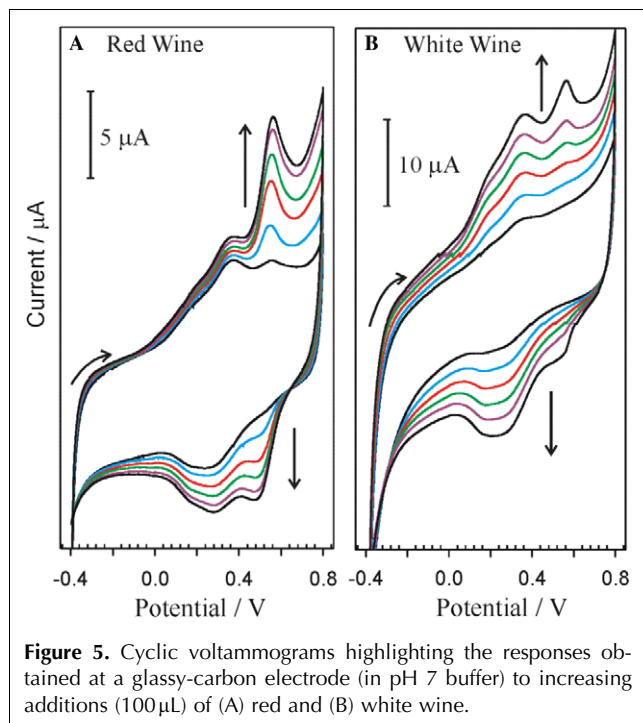
However, problems of selectivity also arise when attempting to quantify sulfite directly in more complex media. The large overpotential required to elicit the oxidation signal can encounter significant interference,
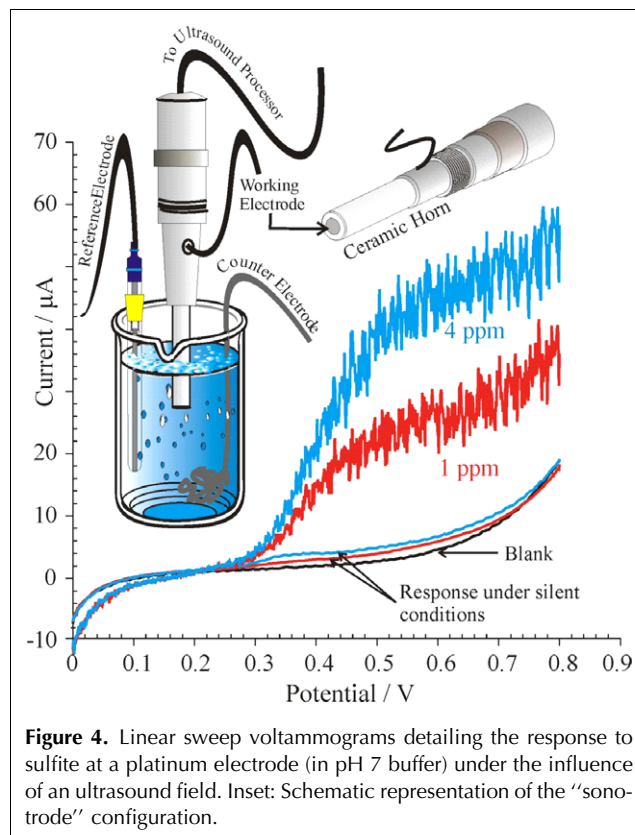
particularly with amperometric systems, where the oxidation of other components will artificially increase the current that would otherwise be attributed solely to sulfite. Ascorbate is invariably the prime suspect when considering electroanalytical detection and almost universally found, at least to some extent, in most biological matrices. Ascorbate is frequently used alongside sulfite as a preservative [21]. The ability of these agents to interfere in the electroanalytical measure is highlighted by the sequential measurement of sulfite and ascorbate.

Wine provides an added complication through the presence of high concentrations of polyphenolics [22–25]. These can also undergo oxidation at similar potentials to sulfite. The voltammetric profile for increasing additions of red and white wine to buffer is detailed in Fig. 5A and B, respectively. A number of distinct electrode processes can be seen and depend on the wine sample being investigated. Nevertheless, these processes inevitably create a degree of ambiguity in ascribing the peak to sulfite or attempting to measure its magnitude. The presence of phenolics, as mentioned in the previous section, is an integral part of wine, irrespective of origin, and they provide a highly variable interferent.

One option that has received little attention is reduction of the anion. In pursuing a cathodic signal, the unwanted oxidation of common interferences could

Figure 5. Cyclic voltammograms highlighting the responses obtained at a glassy-carbon electrode (in pH 7 buffer) to increasing additions (100 μL) of (A) red and (B) white wine.

Figure 6. (A) Linear sweep voltammograms detailing the reduction of sulfur dioxide at a glassy-carbon electrode, and (B) Influence of pH on the voltammetric profile.

easily be avoided. The basis of this approach lies in reduction of dissolved SO_2 and HSO_3^-, the latter resulting in formation of the SO_2^- radical anion [70]. Linear sweep voltammograms highlighting the reduction process are shown in Fig. 6A. The presence of the radical anion has been confirmed by electrochemical electron spin resonance (ESR) measurements and corroborated through the fact that increasing the pH leads to a shift in the peak potential and a sustained decrease in peak magnitude as shown in Fig. 6B. Increasing acidity drives the equilibrium (Equation (3)) to the right-hand side, with the subsequent increase in electro-reducible material.

$$SO_3^{2-} + 2H^+ \rightleftharpoons HSO_3^- + H^+ \rightleftharpoons SO_2 + H_2O \qquad (3)$$
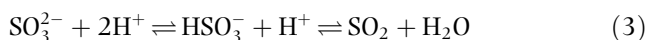
While an unambiguous signal can be obtained at a variety of unmodified electrode substrates (typically carbon or copper), water-soluble cobalt porphyrins have been used to increase the sensitivity of the signal [71]. Again, the responses depend upon an acidic solution. However, it could be difficult to argue the case for adopting the porphyrin systems, given their added complexity compared with simpler and equally viable responses at bare electrodes. In either case, there is one prime interferent – molecular oxygen – which will undergo reduction at the electrode and can obscure the signal due to reduction of the sulfur moieties. Attempts to counter the lack of selectivity obtained at bare electrodes has therefore taken a number of other, more elaborate routes that involve either sample pretreatment (principally the gas-diffusion model) or electrode modification through the incorporation of catalysts (chemical or biological).
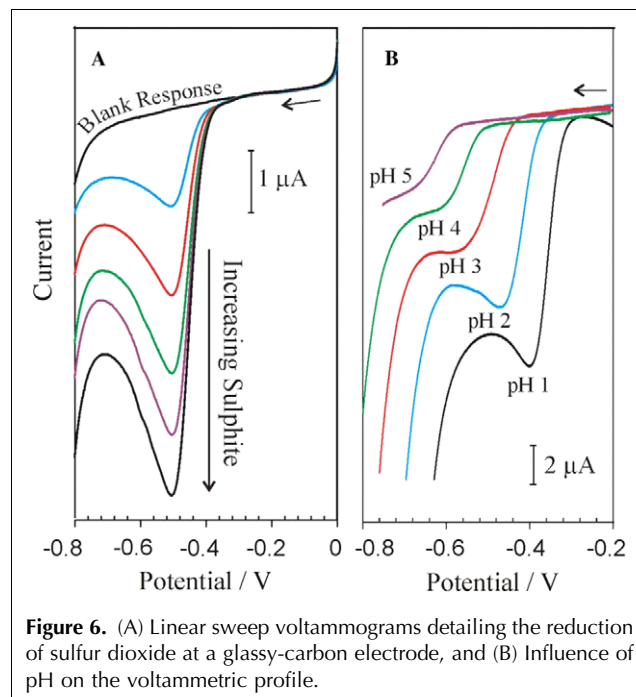
6. Electrode modification

The principal goal in pursuing this pathway is to reduce the potential required to initiate the oxidation of sulfite, thereby minimising the opportunity for unwanted electrode processes (i.e. ascorbate, polyphenolic oxidation) to contribute to the analytical signal. Two approaches are generally followed and involve the use of either metal complexes or biological agents. The former is more common and a variety of complexes have been assessed. These include metallohexacyanoferrate films (Cu, Ni) [72,73], ferrocenes [74], iron phenanthrolines [75,76] and metallophthallocine/porphyrin macrocyles (Ni, Fe, Co) [77–81]. Initially used as solution-based mediators [71,74,75], they are now more commonly immobilised on the electrode as mono or multilayer films or incorporated within the body of composite electrode materials, such as sol gels [82–84].

In many cases, the fundamental electrochemical properties have been investigated with a view to elucidating the various redox transitions within the complex. The reduction of sulfite is normally proffered as a potential analyte but there are few extensive analytical investigations relating to the applicability of the system directly within complex media. While electrode sensitivity to sulfite is invariably increased, it is unclear whether a similar effect would be observed with ascorbate.

The complexes can significantly enhance the current response to sulfite and often succeed in shifting the overpotential for sulfite oxidation to less positive potentials such that the oxidation of polyphenolics could be

avoided. Almost all remain positive of ascorbate oxidation and it could be expected that sample pre-treatment will still be required to eliminate the matrix interferences. Their use as FIA or post-column detectors may have considerable benefits but must be weighed critically in terms of the added complexity of the system. The simple electro-deposition of metals (Cu, CuO and Pt) onto carbon substrates has been shown to enhance detector performance [46,49,63] and could present a more accessible option for the non-specialist operator than the more elaborate complexes.

7. Biosensor designs and operation

The selective redox conversion of sulfite to sulfate can be achieved with a high degree of selectivity through the use of enzymes (sulfite oxidase) [18,54–57,85–91] and microbes (Thiobacillus sp.) [92,93]. A sulfite dehydrogenase has also been investigated, but the lack of commercial availability has restricted its use to more fundamental studies than analytical applications [94]. In general, the bio component can be coupled to conventional electrode substrates and the analytical signal derived from monitoring peroxide oxidation [54,56,85,86], oxygen reduction [87,92,93] or the regeneration of electron-transfer mediators [87–91].

The basic reaction schemes are summarised in Fig. 7. The oxidation of the peroxide by-product (Fig. 7A) is often regarded as the simplest approach but, like direct sulfite oxidation, suffers from the need for large overpotentials. It could be anticipated that enzyme selectivity would therefore be compromised by ascorbate oxidation at the underlying electrode substrate. Coating the electrode with a polymeric film (polytyramine, polydiaminobenzene) onto which the enzyme is then placed has been shown to retain the selectivity [18,85]. In this instance, the polymer acts as a permselective barrier

Figure 7. Reaction schematics highlighting the possible modes through which a sulfite-oxidase enzyme can be integrated within conventional electrode systems.

allowing only the peroxide to reach the electrode. The obvious problem is that imposition of a large potential can stimulate unwanted electrode processes (co-existing interferences) that will contribute to the analytical signal. This route is therefore often employed in conjunction with some form of surface modification to improve the selectivity towards peroxide – which typically means precluding access of most other species to the underlying electrode substrate.

The peroxide by-product can also be reduced (Fig. 7B), with the cathodic potentials avoiding the unwanted oxidation of ascorbate and polyphenols. The main problem that has prevented the adoption of the approach has been the large negative overpotential required to initiate the reduction processes. This can incur oxygen interference and, as mentioned previously, the competing processes will lead to erroneous responses. However, recent investigations have led to the introduction of various surface modifiers capable of catalysing peroxide conversions such that the operating potential of the sensor can be minimised. Common examples are Prussian Blue [95–99] and other mixed metal hexacyanoferrates [100], and electrodeposited metals and alloys (typically Ir/Cu/Pd/Ru [101–103]) and carbon nanotubes [104–106].

The enzymatic process consumes oxygen, and this can be monitored through the electrochemical reduction of oxygen (Fig. 7C) and is the predominant methodology employed when using microbial agents [92,93]. The chief advantage of this route is that the cathodic potentials employed avoid the unwanted oxidation of the matrix interferences. The disadvantage lies in the sensor depending upon ambient dissolved oxygen concentrations and the fact the analytical signal is derived from a decreasing signal rather the positive offset provide by peroxide oxidation. The acquisition of a stable signal is also problematic with the latter providing faster response times. There have been alternative systems, such as potentiometric sensing of oxidase-released peroxide on a field effect transistor-based sensor [57]. The obvious advantage is the microfabrication opportunities afforded by such technology and the inherent capacity for mass manufacture therein.

The dependence on molecular oxygen is removed by using electron-transfer mediators (Fig. 7D), which also remove the peroxide by-product and can allow operating potentials significantly less than those required to oxidise either peroxide or sulfite. Typical examples are TTF-TCNQ conducting salts [88], cytochrome c [89,90] and ferro/ferricyanide [91], which has been used in screen-printed systems with an operating potential of +0.3 V (rel. Ag|AgCl). The influence of ascorbate was not studied, but the technology platform highlights an important step forward when considering the transferability of such systems to small-scale food producers. The underlying technology is essentially the same as that adopted by
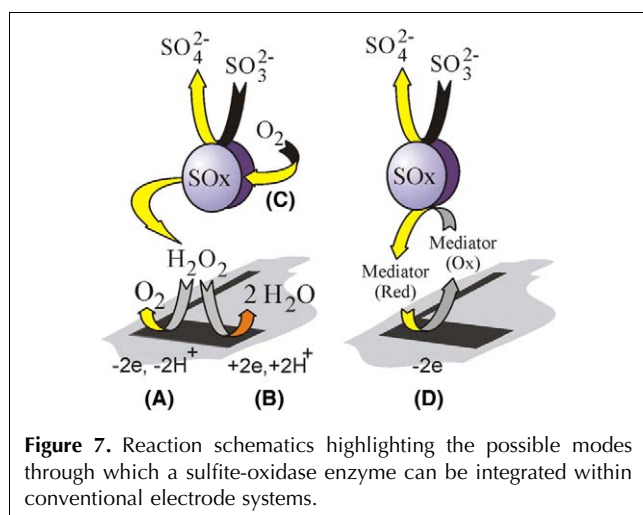
commercial glucose meters and could provide an easily accessible route through which sulfite analysis could be speedily conducted by non-specialist staff. The capability for mass production and the inherent disposability of the sensing strips require little capital outlay or maintenance costs. However, the main proviso is the ability to remove the interference from ascorbate.

8. Potentiometric techniques

Ion-selective electrodes have been widely employed in the food industries for monitoring a range of anions and cations [107,108]. However, there are no commercial sulfite variants. The development of the technology has been restricted largely by the lack of suitable ionophores that are sufficiently selective for the sulfite anion. In principle, this methodology should provide an excellent basis for monitoring sulfite with passive sensing freeing the measurement from the interference effects of ascorbate, urate and the polyphenolics. Interference from other anions is the main problem (particularly perchlorate and salicylates). Membranes based on calixarenes [109], guanidinium [110] and various mercury complexes [111,112] have been the main targets in recent years. The mercury complexes have been shown to function more through redox interactions than specific complexation [112].

Redox indicators have traditionally have been used, though mainly as an alternative to the more classical Monier-Williams titrations with sulfite oxidation by iodine providing the potentiometric trace [9,59]. The main difficulty lies in the reducing properties of ascorbate, which, like sulfite, will reduce iodine. Unless gas distillation/permeation is used to separate these two components [58,59], interference is inevitable.

A more recent approach has involved the use of quinoid indicators [113–115], whose redox properties heavily depend upon the structure and the functionalities of substituents and thus can be tuned to react selectively with sulfite despite the presence of ascorbate. This is highlighted in Fig. 8A, where benzoquinone is shown to respond to additions of not only sulfite but also ascorbate. The change in potential is attributed to the change in the relative ratios of the oxidised/reduced forms of the indicating species and that manifests itself as a change in potential. The greater the concentration of sulfite, the greater the concentration of the reduced species and hence the greater the change in potential.

Changing the indicator to naphthoquinone yields very little response to ascorbate whilst retaining the sensitivity to sulfite [115,116]. The one drawback is that both systems respond to reduced thiols (cysteine, glutathione or sulfide) through classical 1,4-Micheal additions. In contrast to ascorbate, the endogenous presence of such species (particularly sulfide) may be at such low levels as
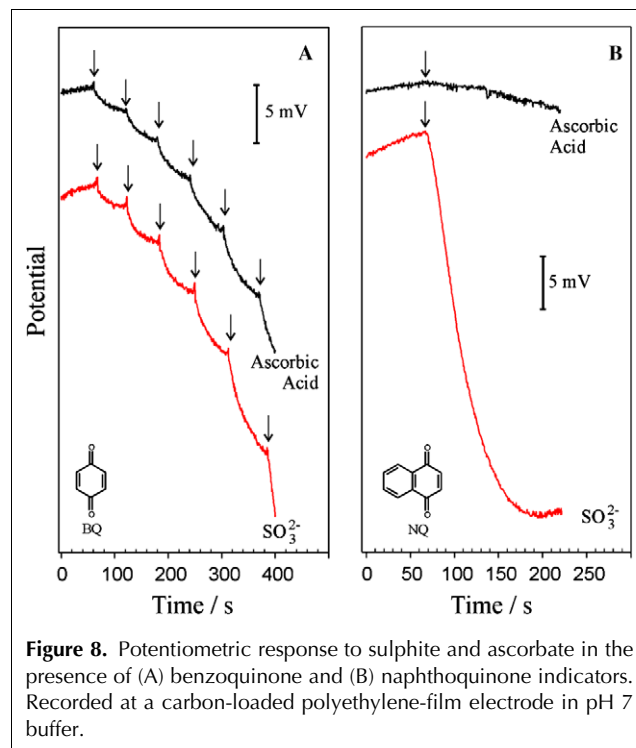
Figure 8. Potentiometric response to sulphite and ascorbate in the presence of (A) benzoquinone and (B) naphthoquinone indicators. Recorded at a carbon-loaded polyethylene-film electrode in pH 7 buffer.

to present insignificant interference to the overall signal. However, it will depend on the nature of the sample being investigated. A key advantage is that the system can be readily adapted to screen-print technologies or to inexpensive composite-electrode materials [115,116].

9. Conclusions

The electrochemical detection of sulfite has traditionally been of fundamental significance to the electrochemical community but it is clear that there is a role for disposable systems in decentralised testing applications. The chief problem in the past has been the interference from other matrix constituents but we have shown that there have been considerable advances in acquiring the necessary selectivity.

The application of complex electrode modifications in the early history of sulfite electroanalysis is evolving to systems that can now be easily transferred to mass-manufacturing processes characterised by screen-print systems. Similar technology has already been demonstrated in the production of simple colorimetric dip strips (Quantofix, Reflectoquant) and offers small producers the capability of assessing sulfite content.

However, these systems may not be suitable for highly coloured or complex media. The quantitative results obtainable through amperometric or potentiometric systems outlined above would clearly be more appropriate for non-expert users – particularly when coupled to the disposable screen-print format, which would offer

a viable alternative to the colour dip tests and conventional laboratory system alike – in terms of simplicity of use, speed of response and, highly important to the small producer, cost.

Acknowledgement

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