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Determination of sulfite by pervaporation-flow injection with amperometric detection using copper hexacyanoferrate-carbon nanotube modified carbon paste electrode

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ABSTRACT

A pervaporation-flow injection (PFI) method was developed for the determination of sulfite in selected food samples using a copper hexacyanoferrate-carbon nanotube (CuHCF-CNT)-modified carbon paste electrode. The electrochemical behavior of the modified electrode was observed using cyclic voltammetry in comparison to a CuHCF-modified carbon paste electrode and a bare carbon paste electrode at a scan rate of 100 mV s^{-1} in 0.10 M KNO_3. The bare carbon paste electrode gave the lowest response to sulfite, while the presence of CuHCF made the detection of sulfite possible through electrocatalytic oxidation by the hexacyanoferrate in the modified electrodes. The presence of CNT in the CuHCF-CNT-modified sensor gave the most remarkable current for the detection of sulfite and was then used as a working electrode in the amperometric flow-through cell in the pervaporation flow injection system. The PFI method involves the injection of a standard or sample sulfite solution into a sulfuric acid donor stream to generate sulfur dioxide gas and evaporate into the headspace of the pervaporation unit. The sulfur dioxide diffuses through the PTFE hydrophobic membrane into a potassium nitrate acceptor stream and reverts to the sulfite form, which, subsequently, is transported to the electrochemical flow cell where it is analyzed amperometrically at a CuHCF-CNT-modified electrode at +0.55 V (vs. Ag/AgCl). The detection was determined to be applicable in the sulfite concentration range of 0.5–50 mg L^{-1}. The sensitivity, detection limit, and sample throughput were determined to be 2.105 nA L mg^{-1}, 0.40 mg L^{-1} and 11 h^{-1}, respectively. The developed PFI method, coupled with the CuHCF-CNT-modified carbon paste electrode, was applied in the determination of sulfite content in sulfite-containing food products. The results agreed well with those obtained through the officially recommended differential pulse polarographic method.

1. Introduction

Sulfites are used as preservatives to prevent oxidation, inhibit bacterial growth, and control enzymatic and non-enzymatic reactions with stabilizing and conditioning functions [1]. Despite these useful advantages, sulfite should be applied in strictly limited amounts due to its potential toxicity. Hence, products containing more than the established threshold sulfite level should be labeled adequately. Due to the allergic effect on hypersensitive individuals such as gastric irritation, nausea, diarrhea, nettle rash or swelling, and asthmatic attacks, sulfite detection has been a study of wide interest [2]. The existence of accurate methods for the determination of sulfites is necessary fundamentally for the food industry to ensure product quality. Previous methods available for determination of sulfites include iodometric titration [3], conductimetry [4], photometry [5,6], chemiluminescence [7], and capillary electrophoresis [8]. Most of these methods, however, need vast sample pre-treatment and solution preparation and result in low specificity and sensitivity in detection. Thus, simpler methods are currently and constantly being studied. Isaac et al. [9] presented an overview of the latest developments in electrochemical procedures for sulfite determination in food and beverages. Decnop-Weever and Kraak [10], Hassan et al. [11], and Tzanavaras et al. [12] have developed flow-spectrophotometric methods for the determination of sulfite in wines and other beverages. Dadamos and Teixeira developed an electrochemical sensor responsible for the electrocatalytic oxidation of sulfite on a platinum electrode modified with nanostructured copper salen (salen = *N*,*N*′-ethylene*bis*(salicylideneiminato)) polymer films [13]. Zhou et al. developed an amperometric sensor based on multi-walled carbon nanotubes/ferrocene-branched chitosan composites

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for the determination of sulfite [14]. Lucero et al. studied the electrocatalytic oxidation of sulfite using a polymeric iron tetra (4-aminophenyl) porphyrin-modified electrode [15]. These developments of sensors for the determination of sulfite all have been of remarkable interest due to a number of advantages brought about by sensors application such as rapid response, high specificity and sensitivity, low cost, and the elimination of sample preparation.

Since their discovery in 1991, carbon nanotubes (CNT) have been of great interest in research; and their various applications have continuously been under study. According to the recent review by Agüí et al., CNT have received great attention for the preparation of electrochemical sensors and biosensors, which based on carbon nanotubes-driven electrocatalytic effects. The construction and analytical usefulness of new hybrid materials with polymers or other nanomaterials were widely reported [16]. Wang et al. previously used multi-walled carbon nanotubes (MWCNT) in the construction of a working electrode by mixing MWCNT with copper powder and mineral oil for use as a capillary electrophoresis detector in carbohydrate determination [17]. Jia et al. developed a new method of constructing a needle-type biosensor based on carbon nanotubes for the detection of glucose [18]. A mixture of MWCNT, graphite powder and glucose oxidase freeze-dried powder was packed into a glass capillary with an inner diameter of 0.5 mm. The resulting biosensor was electrochemically characterized through amperometry–a method that is based on the measurement of electric current at a constant operating potential. The chemical properties of carbon nanotubes, such as enhanced electrical conductivity, chemical inertness, stability, and their capability to promote electron transfer reactions as an electrode with electroactive species in solution, make CNT even more interesting in the application of electrochemical analysis [19,20].

Metal hexacyanoferrates (MHCF) have been a study of wide interest due to their electroactive properties as excellent electron transfer mediators [21]. MHCF have been fabricated using various transition metal cations such as iron [22,23], cobalt [24,25], tin [26], indium [27], silver [28], zinc [29], chromium [30,31], and copper [32–34]. Copper (II) hexacyanoferrate (CuHCF), have been previously investigated to be a good mediator in the catalytic oxidation of sulfite [35], has been used in this study particularly due to the CuHCF mediator's ease of preparation as well as integration into modified carbon paste working electrodes for the determination of sulfite. Ravi Shankaran and Sriman Narayana developed the method utilizing a CuHCF-modified graphite electrode for the amperometric determination of sulfite [35]. Nevertheless, a CuHCF-CNT carbon paste electrode has never been utilized for sulfite determination.

Flow injection analysis of sulfite, coupled with electrochemical detection, has become a method of choice due to the direct electrochemical oxidation of sulfite [22,36–37]. The development of sensors for the determination of sulfite is of remarkable interest due to a number of advantages such as rapid response, high specificity and sensitivity, low cost, and the elimination of sample preparation when it is used with an effective on-line separation technique such as pervaporation [38,39].

In this study, an on-line pervaporation-flow injection (PFI) method, using a highly sensitive CuHCF-CNT electrochemical sensor, was developed for the determination of sulfite in food products where the different aggregation and physical properties of the sample matrices always are a major problem and require sophisticated sample pre-treatment prior to analysis. A pervaporation unit incorporated in the flow system was expected to improve the selectivity while the CuHCF-CNT-modified electrode in an amperometric flow-through cell enhanced the sensitivity of the flow injection system.

2. Experimental

2.1. Reagents and chemicals

All reagents were of analytical grade, and all solutions were prepared using deionized water (Millipore, France). The supporting electrolyte used for the cyclic voltammetry and amperometric determination was 0.1 M KNO_3 (Sigma, USA). The pH of the 0.1 M KNO_3 acceptor stream for the PFI analysis was adjusted using 2.0 M NaOH (Labscan, Ireland) or 2.0 M HCl (Ajax, Australia) solutions where necessary. The 0.050 M H_2SO_4 donor solution was prepared by dissolving the appropriate amounts of concentrated H_2SO_4 (Merck, Germany) in deionized water. Both the donor and acceptor solutions were subjected to ultrasonication before use. A sulfite stock solution (1000 mg L^{-1}) was prepared by dissolving 0.1589 g of anhydrous Na_2SO_3 (J.T. Baker, USA) in 100 ml of deionized water and standardizing by titrating with iodine. This stock solution was kept in a sealed container in a refrigerator at 4 °C when not in use. A series of standard solutions (0.5–50 mg L^{-1}) were prepared using the appropriate dilution of the stock sulfite solution in deionized water.

2.2. Electrode construction

The CuHCF-CNT-modified working electrode was prepared by mixing various ratio compositions of multi-walled carbon nanotube (CNT) (30 ± 15 nm OD, >95% purity, NanoLab Inc., USA), graphite powder ($\leq$20 μm in particle size, synthetic, Aldrich, USA) and mineral oil (Sigma, USA) in an agate mortar. The impure CNT used was previously purified by immersing the tubes in concentrated HNO_3 (Merck, Germany) and subjecting it to ultrasonication for 12 h [35]. The CuHCF mediator was prepared previously by mixing equal volumes of 0.2 M $Cu(NO_3)_2$ (Ajax, Australia) and 0.1 M $K_4Fe(CN)_6$ (Fisher Scientific, UK), heating for an hour in a water bath until the solution dried, and obtaining only the brown CuHCF solid as described previously with slight modification [34]. A portion of each of the resulting carbon pastes was then packed firmly into the cavity of a 3.0 mm diameter Teflon tube (Metrohm, Switzerland) for individual analysis with a stainless steel screw serving as the electrical contact. The resulting electrode surfaces were smoothed using an oil-removing film before examination.

2.3. Apparatus

Cyclic voltammetric and amperometric experiments were carried out using a potentiostat (NSTDA Glucosen Electrochemical Analyzer, Thailand, and CHI1230A CH Instrument, TX, USA). A three electrode system was used with a Platinum wire auxiliary/counter electrode (Sigma, USA), an Ag/AgCl reference electrode (3 M KCl) (CHI111 CH Instrument, TX, USA), and one of the modified carbon paste electrodes as the working electrode.

The amperometric PFI system utilized one two-channeled and one four-channeled peristaltic pump with rate selectors (Gilson, France), one six-port injection valve (Upchurch Scientific, USA), PTFE tubing (TACS, Australia) with an internal diameter of 0.5 mm, and a homemade Perspex pervaporation unit. A flow-through amperometric measuring cell, contained in a Faraday Cage (Autolab, Netherlands), was used for the detection in which the modified carbon paste working electrode was incorporated along with an Ag/AgCl reference electrode (3 M KCl), and a gold counter electrode. Potentials were applied using a potentiostat (791 VA Metrohm, Switzerland) and the detector output was recorded using a portable computer (IBM, Mexico) connected via a USB-RS232 serial port of a digital multimeter (Uni-Trend, Hong Kong).

The pervaporation unit composed of hexagonal donor and acceptor chambers with 0.3 and 5 mm depths, respectively, similar

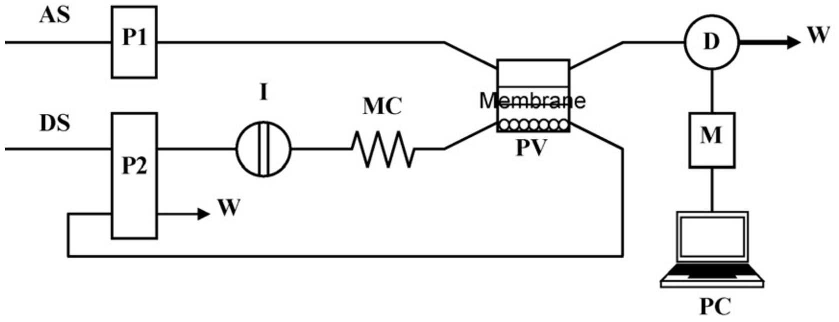

Fig. 1. Schematic diagram of the PFI system used: AS = acceptor solution (0.10 M KNO_3, 2.0 mL min^{-1}); DS = donor solution (0.050 M H_2SO_4, 0.75 mL min^{-1}); P = peristaltic pump; I = sample injection port (300 μL sample injection volume); MC = mixing coil (100 cm); PV = pervaporation unit; D = amperometric flow cell; M = digital multimeter; PC = portable computer; and W = waste.

to that described previously [40]. The donor chamber was packed with a single layer of 3 mm-diameter glass beads for an improved reproducibility and sample throughput [41]. A PTFE membrane (Trace Biotech, Germany) with a thickness of 1.5 mm and a diameter of 4.0 cm was positioned to separate the donor and acceptor chambers to prevent direct contact with the suspended food sample.

2.4. Procedure

The cyclic voltammetric measurements were investigated at a potential range of −0.5 to 1.5 V at 100 mV s^{-1} using the bare, the CuHCF-modified, and the CuHCF-CNT-modified carbon paste working electrodes with 0:80:0:20, 0:70:10:20, and 10:60:10:20 weight compositions of CNT, graphite, CuHCF, and mineral oil, respectively. With the Glucose potentiostat, amperometric measurements of sulfite were carried out at multiple potentials set at 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 V to obtain the current–voltage curves of the modified carbon paste electrodes. A series of 1.2 mM additions of sulfite were injected into the measuring cell containing 2.0 mL of supporting electrolyte and the respective currents were measured amperometrically.

For the PFI analysis, physical and chemical parameters were varied and optimized to obtain optimum results for sulfite detection. The working electrode composition was varied from 0% to 60% CNT, with fixed CuHCF and mineral oil amounts of 10% and 20%, respectively. The amount of graphite used depended inversely on CNT composition in order to retain the correct percentages in the carbon paste.

A 300 μL sample or standard sulfite solution is injected manually via an injection valve into a 0.050 M H_2SO_4 donor stream with the flow rate of 0.75 mL min^{-1} controlled by the first peristaltic pump. The resulting mixture of sulfite solution and the sulfuric donor stream is transported to the donor chamber of the pervaporation unit where it is converted to sulfur dioxide and evaporates into the headspace. Sulfur dioxide gas then diffuses across the PTFE membrane into an acceptor solution containing a 0.10 M sodium nitrate solution. Sulfur dioxide hydrolyses in the acceptor solution and then reverts into the sulfite form, which is transported subsequently to the electrochemical flow cell where it is analyzed amperometrically at a CuHCF-CNT-modified working electrode at +0.55 V (vs. Ag/AgCl). The second peristaltic pump is employed to both propel and withdraw the donor solution from the pervaporation unit; it also assists in the maintenance of a constant liquid

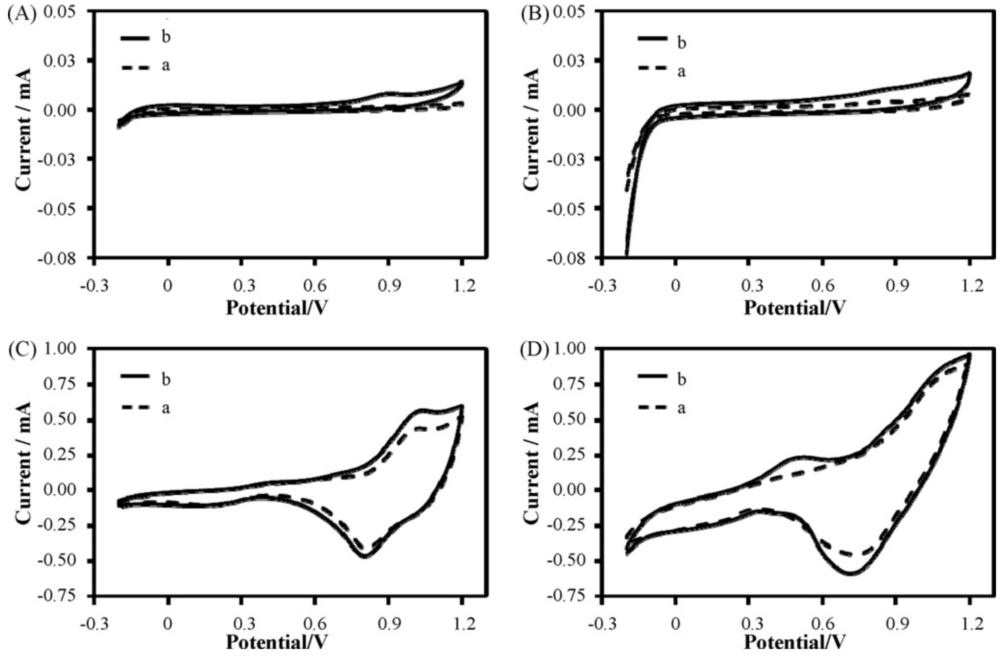

Fig. 2. Cyclic voltammograms for (a) blank and (b) 1.2 mM Na_2SO_3 at (A) bare carbon paste electrode (CPE), (B) CNT-CPE, (C) CuHCF-CPE, and (D) CuHCF-CNT modified electrodes. Supporting electrolyte: 0.1 M KNO_3; scan rate 100 mV s^{-1}.

level in the donor chamber where the glass beads are submerged completely [41].

At the obtained optimized conditions, amperometric PFI measurements were conducted following the scheme shown in Fig. 1. All measurements were carried out at room temperature.

The Association of Official Analytical Chemists' (AOAC) standard differential pulse polarographic method (987.04) [42] was performed using a voltammograph (Metrohm model VA 741, Metrohm Ltd. Switzerland). All samples were acid distillated by purging with oxygen-free nitrogen and collected in an electrolyte-trapping solution (2 M ammonium acetate buffer with 5% ethanol) prior to polarographic analysis.

3. Results and discussion

3.1. Cyclic voltammetric and amperometric measurements

The electrochemical behavior of sulfite towards the proposed CuHCF-CNT modified carbon paste electrode was initially investigated through cyclic voltammetry. Fig. 2 shows the cyclic voltammograms of the four modified working electrodes using a potentiostat. As observed in Fig. 2, voltammograms A (a and b), the magnitude of current detected by the bare electrode was very small with slightly visible response to sulfite oxidation upon addition at about +0.90 V. On the other hand, curve B (a) corresponds to the cyclic voltammogram of the CNT modified electrode in the supporting electrolyte, and curve B (b) with the presence of 1.2 mM sulfite solution. No significant change in the sulfite oxidation peak was observed, indicating that CNT has no effect upon the sulfite catalytic behavior. The CuHCF-modified electrode yields a substantially higher oxidative current over bare and CNT electrodes (notice the different current scales A, B vs. C), and indicates the catalytic oxidation of sulfite by the CuHCF substance. The CuHCF modifier is essential in the catalytic electrochemical oxidation of sulfite, which takes place at the surface of the electrode. Ferricyanide, which is electrochemically generated and present at the electrode surface, chemically oxidizes the sulfite present in the solution into sulfate:

$$\mathrm{Fe(II)(CN)_6}^{4-} \rightarrow \mathrm{Fe(III)(CN)_6}^{3-} + \mathrm{e}^- \qquad (1)$$

$$2\mathrm{Fe(III)(CN)_6}^{3-} + \mathrm{SO_3}^{2-} + \mathrm{H_2O} \rightarrow 2\mathrm{Fe(II)(CN)_6}^{4-} + \mathrm{SO_4}^{2-} + 2\mathrm{H}^+ \qquad (2)$$

While this happens, the electrochemically generated ferricyanide is then reduced to ferrocyanide, which later again becomes electrochemically oxidized [35].

Fig. 2 curves D (a and b) correspond to the cyclic voltammograms obtained using the CuHCF-CNT modified electrode. Even more enhanced anodic currents were achieved using the CuHCF-CNT-modified electrode in blank 0.1 M $\mathrm{KNO_3}$ supporting electrolyte (D (a)) and in the presence of 1.2 mM sulfite (D (b)), respectively, the latter indicating that sulfite was catalytically oxidized by the electrode (the observed oxidative peak at ±0.48 V).

Fig. 3 corresponds to the current–voltage curves obtained for the (a) bare carbon paste, (b) CNT, (c) CuHCF, and (d) CuHCF-CNT modified electrodes in the presence of 1.2 mM sulfite. A series of 1.2 mM sulfite samples were placed into an electrochemical cell and amperometric measurements were taken at 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 V working potentials. A significantly enhanced peak for the CuHCF-CNT-modified electrode may be due to the higher active surface area upon the deposition of CNT into the modified electrode [43] and its unique conductivity properties of CNT [44] made faster electron transfer between CNT and CuHCF.

In addition, a voltage peak shift to the left of the potential axis implies that CNT are more suitable for the detection of sulfite since sulfite is more easily oxidized in the CuHCF-modified electrode presence of CNT.

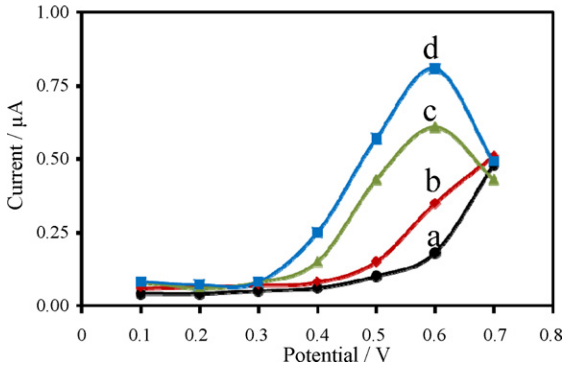

Fig. 3. Current–voltage curves for 1.2 mM $\mathrm{Na_2SO_3}$ in 0.10 M $\mathrm{KNO_3}$ at a (a) bare carbon paste electrode, (b) CNT, (c) CuHCF, and (d) CuHCF-CNT modified electrodes.

3.2. Pervaporation-flow injection (PFI) analysis

After studying its electrochemical behavior, the CuHCF-CNT-modified carbon paste electrode was applied to the amperometric PFI analysis of sulfite. PFI system parameters that affect the sensitivity of sulfite determination were studied. Table 1 lists these parameters including the range over which each parameter was studied and the optimum conditions. The electrode composition of the CuHCF-CNT-modified sensor was optimized by varying the carbon nanotube composition from 0% to 50% (reduce the % graphite from 50 to 0, respectively) and keep the percentage of CuHCF and oil constant. The peak height was measured as the sensor detected a fixed amount of sulfite injected into the system. The current produced with the modified carbon paste electrode without CNT was almost equal to the modified electrodes containing 10 and 20% CNT. The maximum current signal was obtained with the modified electrode containing 30–40% CNT and it keeps plateau until 50% CNT. At these CNT compositions the background current were also high, however, the 35% CNT was giving the highest sensitivity as illustrated by the maximum signal-to-noise ratio. Therefore, the CuCHF-CNT-modified carbon paste electrode was determined to be optimum at an electrode composition of 35% CNT, 35% graphite, 10% CuHCF, and 20% mineral oil.

The criteria for the selection of the optimized parameters include low and stable background current during analysis, and a well-defined peak shape for the detection of sulfite. Best results were obtained in a background acceptor electrolyte which is composed of 0.10 M $\mathrm{KNO_3}$.

The generation of $\mathrm{SO_2}$ gas takes place in an acidic medium and in most gas diffusion-flow injection sulfite determinations; the solution of sulphuric acid is commonly used. The evaluation of the $\mathrm{H_2SO_4}$ concentration, used as a donor stream solution, was carried out over the range 0.025–0.10 M with the flow rate at 0.5 mL min^{-1}. The maximum current was obtained at the concentration of 0.050 M and was considered to be optimal using the univariate approach.

The optimum potential for amperometric detection in pervaporation-flow injection (PFI) analysis was obtained by studying the hydrodynamic voltammetric behavior of sulfite towards the CuHCF-CNT-modified carbon paste electrode. Initially, the range over which the working potential was studied from 0.10 to 1.00 V. However, at very low potentials, very low to zero detection occurred. On the contrary, at very high working potentials, extremely high background noise was observed, hence, lowering the sensitivity of the detection as determined by the signal-to-noise ratio of the injected sulfite standard. Thus, the

Table 1
Pervaporation-flow injection system parameters optimized in this study.

Parameters	Range studied	Optimal value
Acceptor stream composition	0.10 M phosphate buffer (pH 7.0, 7.4); 0.10 M phosphate buffer (pH 8.0)/0.1% SDS; 0.10 M phosphate buffer (pH 7.4)/0.1 M NH_4Cl; 0.10 M phosphate buffer (pH 7.4)/0.01 M Na_2SO_4; 0.10 M NH_4Cl; 0.10 M KCl; 0.10 M KNO_3; 0.10 M KNO_3 and 0.05 M NaOH; 0.10 M KNO_3 and 0.05 M $NaHCO_3$; 0.10 M KNO_3 and 0.01 M NaOH; 0.10 M KNO_3 and 0.01 M $NaHCO_3$	0.10 M KNO_3
Sulfuric acid donor stream concentration (M)	0.025–0.100	0.050
Working electrode composition* (percent CNT by weight)	0–50	35
Electrode potential (V)	0.10–1.00	+0.55
Donor stream flow rate (mL min^{-1})	0.5–2.5	0.75
Acceptor stream flow rate (mL min^{-1})	0.5–3.0	2.0
Sample injection volume (μL)	50–500	300

* The amount of CuHCF and mineral oil added for the construction of the modified working electrode was fixed at 10% and 20% by weight, respectively. The amount of graphite added depended inversely on the amount of CNT used in order to achieve the 100% sample by weight.

working potential range from 0.50 to 0.60 V was more closely evaluated with respect to the peak currents of the injected sulfite standard and the corresponding background currents. The working potential yielded a maximum sensitivity at +0.55 V (versus Ag/AgCl).

The effect of the flow rates of the donor and acceptor streams were studied separately. As expected, the sensitivity was higher at a lower donor stream flow rate but the sample throughput obtained was lower as well. A flow rate of 0.75 mL min^{-1} was then selected to compromise for both the sensitivity and the sample throughput.

As for the acceptor stream flow rate, sample throughput also increased as the rate of flow was increased. The signal detection, however, was highest at a rate of 2.0 mL min^{-1}, and thus, was selected for the acceptor stream flow rate.

Similar to the flow rate, the sample injection volume also affected sensitivity and sample throughput but in the opposite manner. A sample injection volume of 300 μL was selected in resolution to the sensitivity and sample throughput requirements.

3.3. *Analytical figures of merit*

At the optimum working conditions, the calibration curve for sulfite determination was obtained to be linear ($R^2 = 0.9987$) in the concentration range of 0.5–50.0 mg L^{-1}. The linear regression equation in this range can be expressed as $I = 2.105\,C + 5.227$, giving a sensitivity of 2.105 nA mg^{-1} L. A further increase in concentration of the sulfite standards starts to cause a deflection to linearity of the signal with respect to concentration. The limit of detection (LOD), determined experimentally as the lowest sulfite concentration that gives a current signal of three times the background noise, was 0.40 mg L^{-1}. The sample throughput was determined to be 11 h^{-1}.

The compactness of CNT-CuHCF electrode surface is desirable, since it allows the laminar flow in the wall- jet type amperometric flow cell and is detrimental to the reproducibility and lifetime of the sensor. Thus, the sensor is preferably used after being prepared within a day and kept away from open air. The analytical signals corresponding to peak minima were found to be reproducible up to 120 injections (RDS <5%), for the determining of 25.0 mg L^{-1} Na_2SO_3.

In addition, the calibration plot obtained for the determination of sulfite using the developed CuHCF-CNT-modified working electrode was compared to the calibration responses to sulfite using a simple CuHCF-modified carbon paste electrode and a bare glassy carbon electrode as employed in pervaporation-flow injection analysis (Fig. 4). The sensitivity of the developed CuHCF-CNT-modified carbon paste working electrode was the highest at 2.105 nA mg^{-1} L ($R^2 = 0.9987$) compared to the sensitivities of CuHCF-modified carbon paste and bare carbon paste electrodes of 1.043 nA mg^{-1} L ($R^2 = 0.9829$) and 0.029 nA mg^{-1} L ($R^2 = 0.9833$) while the LODs for the other two electrodes were found to be 1.5 mg L^{-1} and 10 mg L^{-1}, respectively.

Table 2
Tolerance limits of possible interferences in the PFI method.

Tolerance ratio*	Interferences
1:100	Na^+, K^+, Ca^{2+}, Zn^{2+}, Cl^-, CH_3COO^-
1:10	Mg^{2+}, Ni^{2+}, $SO_4{}^{2-}$, $HPO_4{}^{2-}$, sucrose
1:1	Fe^{3+}, Mn^{2+}, Co^{2+}, ascorbic acid
1:<1	I^-

* The tolerance ratio indicates how much equivalent interference (I) concentration can be tolerated per 25.0 mg L^{-1} Na_2SO_3 control (C) in this manner: C: I.

3.4. *Interference study*

Possible interferences of food matrices to the PFI method were studied. The tolerance ratios of possible coexisting ions and compounds are listed in Table 2. The values were determined using 25.0 mg L^{-1} Na_2SO_3 as the control and tolerance was based on whether the interference causes an error of greater than 5%. Table 2 indicates that up to 100 times the Na_2SO_3 control can be tolerated for interferences such as sodium and chlorine; however, only equal amounts of other interferences such as iron and ascorbic acid can be tolerated and even less of iodine. The results can be attributed to the unique chemical property of the carbon nanotubes, its enhanced electrical conductivity, making it highly sensitive to the presence of ions which also possess redox properties, if such species could

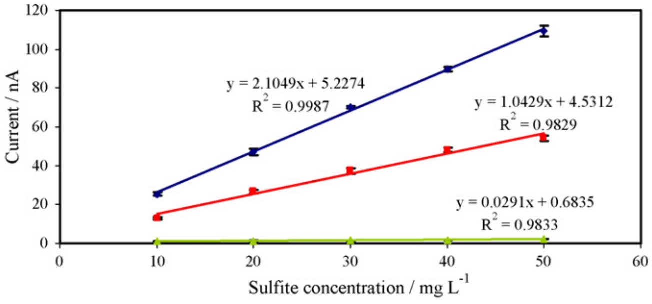

Fig. 4. Calibration curves of sulfite with (-◇-) CuHCF-CNT, (-●-) CuHCF, and (-Δ-) bare carbon paste working electrodes.

Table 3
Comparison of results obtained by PFI and DPP methods for sulfite in pickled food.

Sample	Sulfite content ($mg\,kg^{-1}$)		Percentage recovery for proposed PFI method
	PFI method	DPP method	
Bean spout	162 ± 3	154 ± 5	96.8–104.6
Pickled cabbage	110 ± 1	102 ± 4	97.5–102.9
Pickled bamboo shoot	27.0 ± 0.4	26 ± 2	96.2–101.9
Pickled ginger	23.1 ± 0.5	25 ± 3	97.5–104.8

Standard deviation calculated on the basis of three replicate measurements.

reach the electrode surface. However, these species were found to suppress the analytical signals as the concentration ratios were increased. This can be explained by the redox character of these species resulting in lower production of volatile SO_2 in the donor chamber, particularly with the I^- interference. Higher concentrations of the interfering species in the standard solution may also hinder sulfite from evaporating into sulfur dioxide gas, hence, hindering the detection of the genuine concentration of the analyte by the PFI system. Therefore, sulfite standard solutions containing higher concentrations of the interfering ions caused significant interference affecting the sulfite detection.

3.5. *Real sample analysis*

The developed PFI method was applied to the determination of sulfite in pickled food samples in order to evaluate the accuracy of the proposed PFI system. The sulfite concentration present in each pickled food sample was measured by standard addition method. A 50 g of each sample was weighed and was homogenized with an equivalent volume of deionized water. The resulting homogenized mixture was collected and served as the sample stock solution. A series of increasing concentrations from 5.0 to 25.0 $mg\,L^{-1}$ of standard sulfite solution were next prepared containing equivalent amount of the sample stock solution and was diluted to mark with the donor solution (0.025 M H_2SO_4 solution). These prepared solutions were consecutively injected into the PFI system for analyzes.

The results were then compared with those obtained using differential pulse polarography (DPP), which is the standard method for sulfite determination as proposed by the Association of Official Analytical Chemists (AOAC) [42]. The results obtained by both methods, including the percentage recovery upon addition of certain amounts of standard sulfite solution, are shown in Table 3. The relative standard deviations for the analysis of sulfite in pickled food samples using the proposed PFI method were in the range of 1.0–2.2%.

The Student's *t*-test was also calculated for both methods at 98% confidence [45]. After comparing the calculated *t* values of each food sample obtained from PFI with the AOAC method, results revealed that the data obtained using the developed PFI method with the CuHCF-CNT-modified working electrode was reliable.

4. Conclusions

The presence of CuHCF made the detection of sulfite possible through the electrocatalytic oxidation of sulfite by hexacyanoferrate in the modified electrode. Moreover, the presence of CNT in the modified sensor gave an even more remarkable effect for the detection of sulfite. This promising result led to the fabrication of an amperometric flow detector for sulfite in a flow system.

CuHCF-CNT modified electrode is more effective in the determination of sulfite in aqueous solution as compared to the use of bare carbon paste or a CuHCF-modified carbon paste electrode. The developed electrode was successfully applied to pervaporation-flow injection analysis as an effective sensor for sulfite determination, allowing a higher selectivity during sulfite analysis and producing a good sensitivity and a relatively low detection limit. Using versatile designs of the pervaporation unit, food samples containing many matrices can be analyzed more selectively. Compared with the method based on photometric PFI proposed by Mataix and Luque de Castro [38] the current proposed method requires a less-complicated set-up and provides a wider linear range and lower detection limit. The proposed PFI method is also applicable in the analysis of real pickled food samples obtaining reliable results as compared to the standard method of sulfite determination.

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