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Aurelia Magdalena Pisoschi*, Aneta Pop

Comparative sulfite assay by voltammetry using Pt electrodes, photometry and titrimetry: Application to cider, vinegar and sugar analysis

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Abstract: Sulfite is a widely applied preservation agent, against oxidative decay in foodstuffs and beverages. Among the analytical methods applied, electrochemical techniques exploit its facility to undergo oxidation. This paper aims at the comparative investigation of the performances exhibited by three analytical methodologies: cyclic voltammetry at different Pt working electrodes, the volumetric method employing sodium thiosulfate as titrating agent and the photocolorimetric method relying on the reduction of Fe^{3+}-orthophenanthroline complex by sulfite. The cyclic voltammetric assay was performed at Pt strip and Pt ring electrodes, by linearly sweeping the potential between -100 and 1,500 mV. The linear range corresponded to 7.5 mg L^{-1} – 4.0 g L^{-1} for Pt strip working electrode and to 15.5 mg L^{-1} – 4.0 g L^{-1} for Pt ring working electrode. Relative standard deviations smaller than 3% showed repeatability. RSD values smaller than 3% were also obtained in the photometric assay, but the latter was characterised by a narrower linear range. The Pt strip electrode allowed wider linear range and lower sensitivity, whereas the Pt ring electrode with Ag/AgCl reference in the same unit was characterised by better repeatability. Applications involved sulfite assay in vinegar, brown sugar and cider samples with consistency between cyclic voltammetry and titrimetry.

Keywords: Sulfite food assay; cyclic voltammetry; Platinum electrodes; orthophenanthroline photometry; thiosulfate titrimetry.

1 Introduction

Sulfite represents a preservation agent widely applied in foods and drinks to hinder the oxidative decay of their components. Sulfite is characterised by means of its reductive properties, as it can be easily oxidized to sulfate [1]. Sulfites are incorporated in: processed meats, wines, beer and cider, soft drinks and fruit juices, jams and jellies, dried and pickled fruits and shellfish [1]. Developments in analytical methodologies are required, namely for chemical compounds present in food, that may constitute a safety risk [2].

WHO/FAO, through Codex Alimentarius, Codex Stan [3] lists sulfites among the major allergens, and the European Union as well, through the Regulation (EU) 1169 [4]. The latter stipulates the presence of the allergens on the label of the product, and in the case of sulfur dioxide and sulfites, for concentrations greater than **10 mg kg^{-1} or 10 mg L^{-1}, as SO_2**.

The term “sulphites” encompasses collectively sulfur dioxide (INS 220), sodium sulfite (INS 221), sodium bisulfite (INS 222), sodium metabisulfite (INS 223), potassium metabisulfite (INS 224), potassium sulfite (INS 225) [3].

The first renowned method for sulfite assay is Monier-Williams titrimetry [5], later modified for the use in food and beverages [6]. Redox titration with iodine solution, after distillation, was another method applied to assess the concentration of sulphites [7]. High performance liquid chromatography was also applied, and employed a HPX-87H column with diode array detection. The sulfuric acid concentration in the eluent solution was comprised between 0.0025 N and 0.06 N [8].

Spectrophotometric sulfite assay can rely on the reaction of pentacyanidonitrosylferrate(II) and sulfite anion. The nitroprusside-SO_3^{2-} reaction product was stabilized by zinc ethylenediamine complex and the absorbance was measured at λ = 482 nm. The repeatability was 2.37% and the obtained limit of detection was 0.99

***Corresponding author: Aurelia Magdalena Pisoschi,** University of Agronomic Sciences and Veterinary Medicine of Bucharest, Faculty of Veterinary Medicine, 105 Splaiul Independentei, 050097, sector 5, Bucharest, Romania, E-mail: aureliamagdalenapisoschi@yahoo.ro
Aneta Pop: University of Agronomic Sciences and Veterinary Medicine of Bucharest, Faculty of Veterinary Medicine, 105 Splaiul Independentei, 050097, sector 5, Bucharest, Romania

µg mL^{-1} SO_3^{2-}. The results of the photocolorimetric assay were compared with those obtained iodometrically, by subjecting excess iodine to titration with thiosulfate in the presence of starch [9]. Photocolorimetric sulfite assay can also be based on SO_2 reaction with Schiff's **fuchsin reagent** [10,11]. The modified para-rosaniline-formaldehyde method exhibits broad linear range (0.05–5.0 mg L^{-1} as SO_2), whereas the 5,5′-dithiobis(2-nitrobenzoic acid) method, operates within a linear range of 0.10–4.30 mg L^{-1} SO_2 [12].

Electrochemical methods have the advantages of accuracy, rapidity, and low cost, when compared to other time-consuming instrumental methods [13]. Voltammetric and polarographic methods are applied to determine sulfur-containing preservatives [14,15]. Sulfite electroactivity consists in its propensity to undergo facile oxidation to sulfate, and allows for its quantitation by electrochemical techniques, namely voltammetry, amperometry, potentiometry.

Cyclic voltammetry relies on linearly sweeping the potential, the analytical peak being due to sulfite oxidation to sulfate and the oxidation of sulfite was investigated at platinum electrodes [16-18]. The irreversibility of the process is proved by studies performed at the surface of a graphite electrode, in alkaline media [19]. With respect to the electro-oxidation steps, it was stated that: either sulfite anion can be oxidized to sulfate in two consecutive steps, each implying one electron transfer [20,21],

$$\begin{aligned} SO_{3\ aq}^{2-} &\rightarrow SO_{3\ aq}^{\bullet -} + e^- \\ SO_{3\ aq}^{\bullet -} + 2\,OH_{aq}^{-} &\rightarrow SO_{4\ aq}^{2-} + H_2O + e^- \end{aligned}$$

or sulfite anion can undergo one step oxidation (one electron transfer) to sulfite radical anion. Subsequently two sulfite anion radicals react, resulting in dithionate anion $S_2O_6^{2-}$occurrence. The latter disproportionates, giving sulfate and sulfite [20,21].

$$\begin{aligned} SO_{3\ aq}^{2-} &\rightarrow SO_{3\ aq}^{\bullet -} + e^- \\ 2\,SO_{3\ aq}^{\bullet -} &\rightarrow S_2O_{6\ aq}^{2-} \\ S_2O_{6\ aq}^{2-} + 2\,OH_{aq}^{-} &\rightarrow SO_{3\ aq}^{2-} + SO_{4\ aq}^{2-} + H_2O \end{aligned}$$

In cyclic voltammetric studies at a carbon paste electrode modified with carbon nanotubes and p-aminophenol, sulfite oxidation was reported to take place at 680 mV. The analytical peak due to electro-oxidation depends linearly on concentration for 2x10^{-7}- 2.8 x10^{-4} mol L^{-1}, allowing for accurate determination in residual waters [22].

Square-wave voltammetry using carbon nanotubes-modified carbon paste electrode allows for quantitation of this preserving agent in beverages. The analytical range of linear response corresponds to 25.0–500.0 µmol L^{-1}, with a detection limit of 1.0 mg L^{-1} SO_2 (at 16 µmol L^{-1} sulfite) [23].

Simultaneous voltammetric assessment of ascorbic acid and sulfite in beverages, was performed at a glassy carbon electrode modified with multi walled carbon nanotubes and polyallylamine [24].

Using cobalt layered perovskite or skeletal nickel as electrode material in fuel cells, allows for sulfite direct oxidation at the electrode surface [25,26]. A comparative study using three glassy carbon electrodes modified by Co-porphyrin, ortho-phenylendiamine, or both, simultaneously, allowed for sulfite electro-oxidation in 0.02 mol L^{-1} NaOH solution. A concentration of 44.0 µg mL^{-1} of free sulfite was assessed in a Chilean red wine, by standard addition method [27].

Modification of a Pt electrode with carbon nanotubes and Prussian Blue led to the amperometric assay of sulfite (at 600 mV) in the presence of iodate and periodate, with a linear range of 16.4 - 142.9 µmol L^{-1} [28]. A novel system comprising a flow gas diffusion unit and a wall-jet amperometric FIA detector, coated with a supra-molecular porphyrin film, allowed fast, reproducible and accurate assay of free sulfite in fruit juices, with optimization of analytical parameters: linearity range 0.64 - 6.4 µg mL^{-1} sodium sulfite, detection limit of 0.043 µg mL^{-1}, a RSD of +/- 1.5% (n = 10) and an analytical frequency of 85 analyses per hour [29].

Biosensors combine the rapidity of electron transfer with the specificity of the biocatalyst [13, 30]. Sulfite oxidase-based biosensors can be developed by enzyme immobilization in a Prussian Blue nanoparticles/polypyrrole composite matrix, electrodeposited on an indium oxide electrode [31]. Recently, sulfite oxidase was also immobilized on a magnetite-gold-folate nanocomposite modified carbon-paste electrode. The linearity range corresponded to 0.1-200 mg L^{-1}, with a detection limit of 10 µg L^{-1}, proving enhanced electro-activity towards H_2O_2 resulted in the enzymatic substrate oxidation [32]. A flow injection biamperometric assay relying on the redox reaction between the I^{3-} and SO_3^{2-} ions, enabled a linear response ranging from 1.0 to 12.0 mg L^{-1} [33].

This study aims to investigate the performances in sulfite determination, of cyclic voltammetry at Pt strip and Pt ring electrodes, sodium thiosulfate titrimetry, and Fe^{3+}-orthophenanthroline photocolorimetry. This research deals comparatively with the application of three analytical techniques for sulfite assay, which imparts the degree of novelty to the present study. Real sample analysis consisted in sulfite assay in vinegar, brown sugar and cider samples.

2 Experimental procedure

2.1 Reagents and apparatus

To achieve the objective of this study, a KSP potentiostat-galvanostat („built in house" by Professor Slawomir Kalinowski, University Warmia and Mazury, Olsztyn, Poland), as well as the respective software Cyclic Voltammetry for recording the cyclic voltammograms, and a three-electrode voltammetric cell, with a working, a counter and a reference electrode were used.

As working electrodes a Pt strip electrode Radelkis OP-0612P (30 mm^2 surface) and an Oxidation Reduction Potential (ORP) Pt ring electrode Mettler-Toledo Pt 4805-DPA were handled. The Pt electrode Mettler-Toledo Pt 4805-DPA had an Ag/AgCl reference incorporated in the same unit.

In addition, a saturated calomel reference electrode (SCE), Radelkis was only used when the working electrode was the Pt strip (Radelkis OP-0612P 30 mm^2 surface) and finally the counter electrode was a always Pt strip Radelkis OP-0612P.

Standard solutions of sodium sulfite (Na_2SO_3 anhydrous p.a., Chimopar Bucharest, Romania) with concentrations ranging between 5 mg L^{-1} and 5 g L^{-1}, were freshly prepared before every determination. KCl (Chimopar Bucharest, Romania) as 0.1 mol L^{-1} solution (pH=6.5) was used as supporting electrolyte for all standards preparation.

2.2 Working procedure

Before every determination, both Pt working electrodes were cleaned mechanically on alumina slurry and electrochemically by applying a -1.5 V potential pulse for 3 seconds.

The volume of the analysed sodium sulfite solution was 50 ml and all measurements were performed at 24^{0}C, using a 0.10 mol L^{-1} KCl solution as supporting electrolyte.

For the cyclic voltammetry measurements, the potential was scanned within the range -100 to 1,500 mV, at a 50 mV s^{-1} scan rate. For the investigation of the influence of the scan rate, this parameter varied between 25 and 250 mV s^{-1}.

The voltammetric determinations were performed at 5 minutes after standard sulfite solution preparations, using 0.1 mol L^{-1} KCl as electrolyte, in order to hamper the confirmed rapid analyte oxidation [34].

For titrimetric sulfite assay, to 50 mL sample (vinegar, cider), 5 mL iodine solution 0.1 N were added, followed by titration with a thiosulfate solution 0.1 N, in the presence of starch.

$$I_{2\,aq} + 2\,Na_2S_2O_{3\,aq} \rightarrow Na_2S_4O_{6\,aq} + 2\,NaI_{\,aq}$$

The volume used is equivalent to excess iodine, so sulfur dioxide or sodium sulfite amounts can be calculated as per the reference to their equivalents:

$$g\ SO_2/\text{sample} = (V_{I2}\ x\ F_{I2} - V_{Na2S2O3}\ x\ F_{Na2S2O3})\ x\ 0{,}1\ \ x\ \ mEg_{SO2}$$
$$g\ Na_2SO_3/\text{sample} = (V_{I2}\ x\ F_{I2} - V_{Na2S2O3}\ x\ F_{Na2S2O3})\ x\ 0{,}1\ \ x\ \ mEg_{Na2SO3}$$

In the case of brown sugar, to 15 mL brown sugar solution (that contained 10 g sugar), 1.5 mL iodine solution 0.1 N were added, followed by thiosulfate titration.

For the photometric assay, to 1 mL complex solution, the appropriate volume of a 200 mg L^{-1} sulfite solution was added. Then distilled water was addded, to the final volume of 10 mL. The final concentration in the analysed standard solutions was comprised between 10 and 100 mg L^{-1}. Readings were performed at λmax = 515 nm.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Disscussion

3.1 Comparative investigation of analytical parameters

A series of cyclic voltammograms, at sulfite concentrations ranging between 5.0 mg L^{-1} and 5.0 g L^{-1} were recorded using alternatively the Pt strip electrode and the Pt ring electrode with Ag/AgCl reference electrode. The most representative cyclic voltammograms are presented in Figures 1-3. The observed oxidation potentials between 500 and 1000 mV vs saturated calomel or Ag/AgCl references were comprised within the ranges reported in literature [18].

The variation of the anodic peak with the increase of the potential scan rate was investigated. The electroactive process is diffusion-controlled, which is proven by the linear dependence of the current intensity on the square-root of the potential-sweep rate (Figure 4), which is in agreement with Randles-Sevcik law. It could be concluded that the value of the measured current intensity is controlled by the analyte diffusion from the bulk solution to the electrode/solution interface.

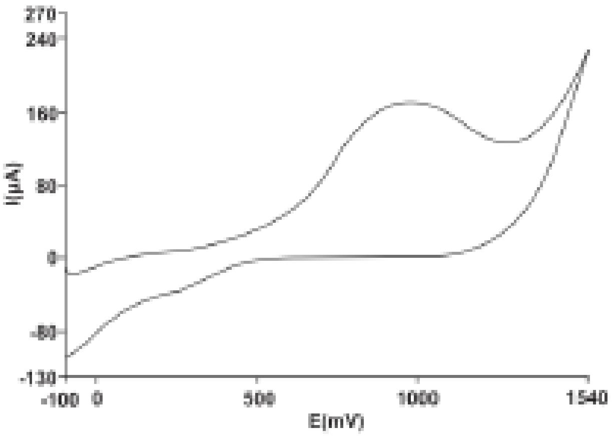

Figure 1: Cyclic voltammogram obtained at the Pt strip electrode Radelkis, for 250 mg L^{-1} sulfite using as electrolyte 0.1 mol L^{-1} KCl; scan rate=50 mV s^{-1}

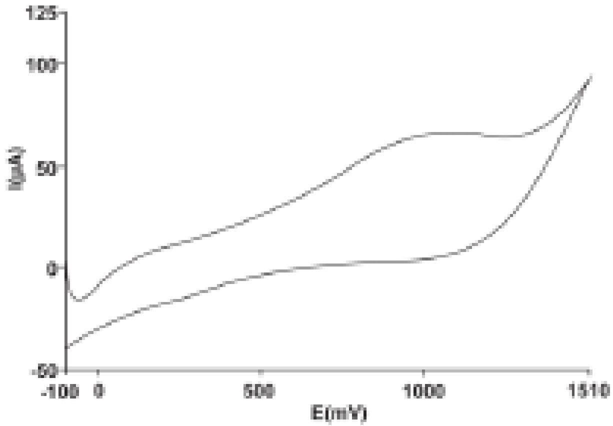

Figure 2: Cyclic voltammogram obtained at the Pt strip electrode Radelkis, for 62.5 mg L^{-1} sulfite using as electrolyte 0.1 mol L^{-1} KCl; scan rate=50 mV s^{-1}

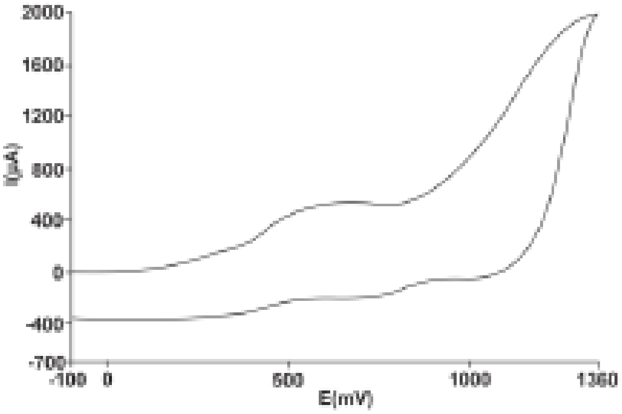

Figure 3: Cyclic voltammogram obtained at the Pt ring electrode Mettler-Toledo, for 500 mg L^{-1} sulfite using as electrolyte 0.1 mol L^{-1} KCl; scan rate=50 mV s^{-1}

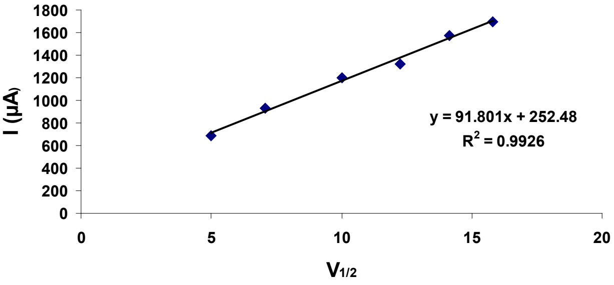

Figure 4: Illustration of the dependence of the current intensity on the square root of the potential sweep rate, studied between 25 and 250 mV s^{-1}, at 1.5 g L^{-1} sulfite concentration

The influence of the scan rate was studied between 25 and 250 mV s^{-1}. For the standard solutions as well for real sample assay, we chose a 50 mV s^{-1} scan rate, fast enough to ensure analyte diffusion to the electrode (determined by the concentration gradient between bulk solution and electrode surface) and electron transfer facility. In the case of irreversible or quasi-reversible electron transfers, at high scan rates, the electron transfer becomes slow relative to the potential sweep rate, and the rate of establishing the equilibrium at the electrode surface is lowered. Under these circumstances, the analyte concentrations generated at the surface of the electrode are not consistent to those estimated by Nernst dependence. Moreover, very elevated scan rates generally result in peaks characterised by high current intensities, but distortions may appear on the voltammogram.

The developed calibration curves (Figures 5, 6) showed a linear range of analytical response corresponding to 15.5 mg L^{-1} – 4.0 g L^{-1} for the Pt ring electrode and to 7.5 mg L^{-1} – 4.0 g L^{-1} for the Pt strip electrode. The details at concentrations below 1 g L^{-1} are given in figures 7 (Pt ring electrode) and 8 (Pt strip electrode) respectively.

The equations of the calibration graphs on the whole linear analytical range corresponded to y = 525.07x + 63.74, with a correlation coefficient R_1^2 = 0.9906 for the Pt strip electrode, and y = 454.78x + 163.44, with a correlation coefficient R_2^2 = 0.9921, for the Pt ring electrode respectively, where y represents the value of the current intensity, and x the analyte concentration. Hence, the sensitivity given by the slope of the linear dependence was greater for the Pt strip electrode than for the Pt ring electrode with Ag/AgCl reference incorporated.

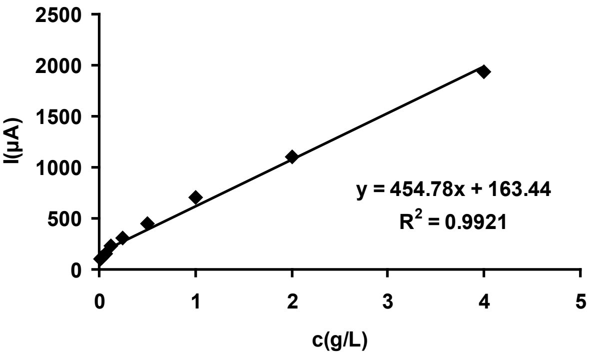

Figure 5: The calibration graph, as current intensity versus sulfite concentration dependence, obtained with the Pt ring electrode Mettler-Toledo

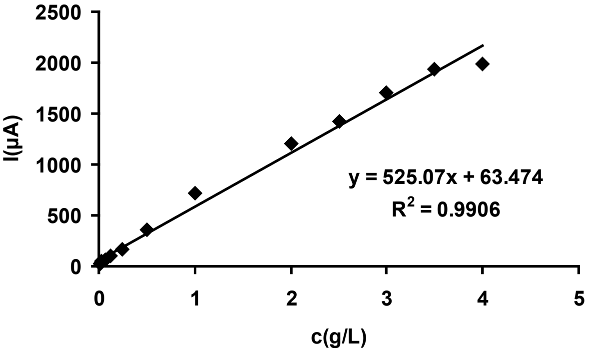

Figure 6: The calibration graph, as current intensity versus sulfite concentration dependence, obtained with the Pt strip electrode Radelkis

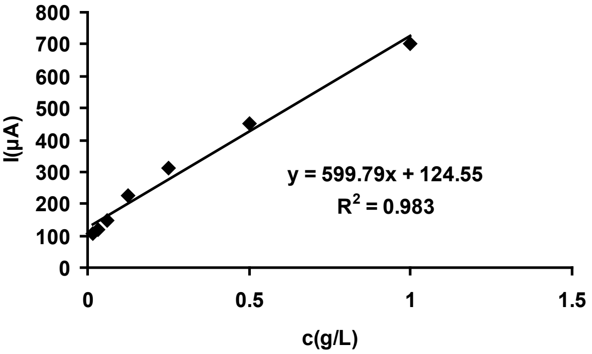

Figure 7: Detail on the calibration graph at sulfite concentrations below 1 g L^{-1}, obtained with the Pt ring electrode Mettler-Toledo

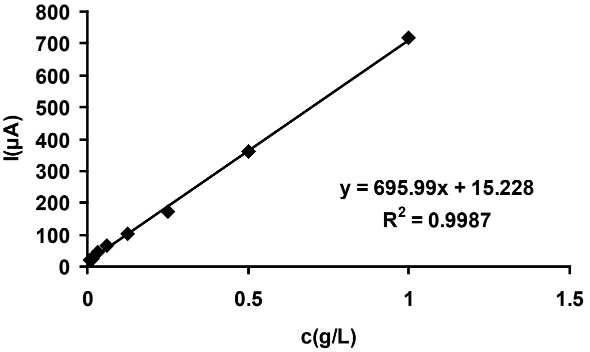

Figure 8: Detail on the calibration graph at sulfite concentrations below 1 g L^{-1}, obtained with the Pt strip electrode Radelkis

The equations of the calibration graphs below 1 g L^{-1} corresponded to y = 695.99x + 15.228, with a correlation coefficient $R_1^2 = 0.9987$ for the Pt strip electrode, and y = 599.79x + 124.55, with a correlation coefficient $R_2^2 = 0.9830$, for the Pt ring electrode respectively, showing a greater sensitivity for the Pt strip electrode.

The precision of the voltammetric assay, as illustrated by the values of the relative standard deviation, was tested for both electrodes. The RSD values were calculated as:

RSD = 100 x SD / mean of determinations

The value of the relative standard deviation (RSD) was 2.68%, with 0.004022 standard deviation (SD) for the Pt strip electrode. The value of the relative standard deviation (RSD) was 2.55%, with 0.003806 standard deviation (SD) for the Pt ring electrode. To assess these analytical parameters, n=10 determinations were performed, at c = 0.15 g L^{-1} sodium sulfite, exploiting the dependence at small (below 1 g L^{-1}) concentrations.

Moreover, RSD values were calculated for both electrodes, at c = 1.0 g L^{-1} sodium sulfite (n=10), exploiting the dependence on the whole linear analytical range: the RSD value was 2.54%, with 0.02565 standard deviation (SD) for the Pt strip electrode. The RSD value was 2.46%, with 0.02505 standard deviation (SD) for the Pt ring electrode.

The results obtained were comparable to those obtained in other studies with respect to repeatability illustrated by RSD [9,22].

The detection limits were 1.908 mg L^{-1} for the Pt strip electrode and 3.168 mg L^{-1} for the Pt ring electrode, respectively. The limit of detection was calculated as:

LOD = 3.3 s/m [35],

where ***s*** represents the standard deviation corresponding to the blank (KCl 0.1 M electrolyte solution) signal, and ***m*** represents the slope of the calibration graph below 1 g L^{-1},

Table 1: The results obtained at sulfite analysis in cider, vinegar and brown sugar samples.

Analysed product	**mg SO_2/L**		**mg Na_2SO_3/L**	
	titrimetry	**voltammetry**	**titrimetry**	**voltammetry**
Apple cider Elderflower	153.60±4.65	161.35±4.28	302.40±9.15	317.66±8.43
Apple cider Golden apple	51.20±1.65	55.46±1.42	100.80±3.25	109.18±2.80
Apple cider Redberries	96.0 ± 2.78	102.74±2.83	189.0±5.31	202.26±5.58
Vinegar (origin Greece)	76.80± 2.18	78.87±1.85	151.20±4.29	155.27±3.65
Vinegar (origin Romania)	44.80 ± 1.29	46.52±1.09	88.20±2.54	91.58±2.15
Brown sugar (origin Mauritius)	18.82 ± 0.53 mg/kg	19.27± 0.46 mg/kg	37.05±1.04 mg/kg	37.94±0.91 mg/kg

considered for each electrode: 695.99 µA g^{1} L for Pt strip and 599.79 µA g^{1} L for Pt ring.

The limits of quantification were 5.781 mg L^{-1} for the Pt strip electrode and 9.60 mg L^{-1} for the Pt ring electrode, respectively. The limit of quantification was calculated as:

$$LOQ = 10\ s/m,$$

where ***s*** and ***m*** have the same significance as before [35]. The calibration graph developed at the photometric sulfite assay based on the reduction of Fe^{3+}-orthophenanthroline complex is presented in Figure 9, with a linear range of 10-80 mg L^{-1}.

The spectrophotometric assay was characterised by a standard deviation (SD) of 0.7261 and a relative standard deviation (RSD) of 2.89% (at c= 25 mg L^{-1} sulfite concentration, n=10 determinations), and a limit of detection of 2.915 mg L^{-1}.

3.2 Analytical applications on some real samples

Table 1 presents the results obtained at sulfite analysis in samples of cider, vinegar and brown sugar, that were obtained by applying cyclic voltammetry at Pt strip electrode (with better sensitivity and detection limit), and comparatively, the thiosulfate titrimetry.

The application of the standard addition method in vinegar is illustrated in Figure 10.

The application of the standard addition method in elderflower cider is illustrated in Figure 11.

3.3 Statistical analysis

A Student's t-test was performed, to statistically analyse the differences between the mean concentrations

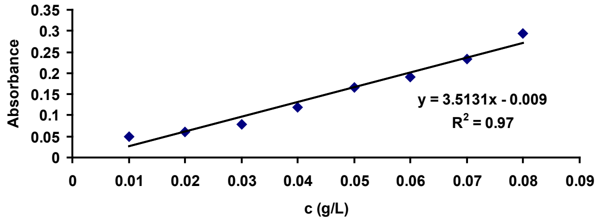

Figure 9: The calibration graph, as absorbance versus sulfite concentration dependence, developed at the photometric assay based on the reduction of Fe^{3+}-orthophenanthroline complex.

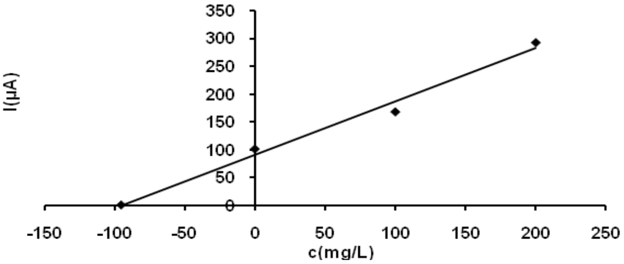

Figure 10: The application of the standard addition method in vinegar. The obtained concentration, 95.1 mg L^{-1} as sodium sulfite is in accordance with the one obtained by direct voltammetry, illustrating accuracy.

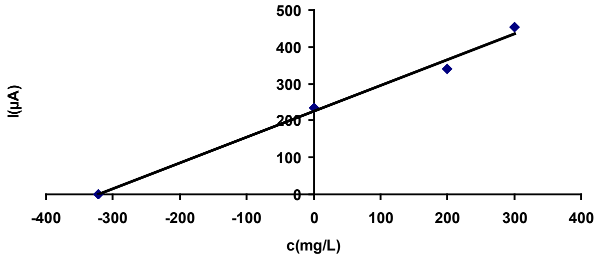

Figure 11: The application of the standard addition method in elderflower cider. The obtained concentration, 321.28 mg L^{-1}, as sodium sulfite, is in accordance with the one obtained by direct voltammetry, illustrating accuracy.

obtained by the two methods, with respect to sulfite concentration (Table 2). The t-values are presented, as well as the confidence levels for which there are no statistically significant differences between the mean concentrations given by the two methods ($t_{calculated} < t_{tabulated}$). The statistical analysis relied on a two-tailed test. It was performed for eight degrees of freedom (df), as n_1=5 (voltammetry) and n_2=5 (titrimetry). Hence:

$$df = n_1 + n_2 - 2 = 5 + 5 - 2 = 8$$

For two of the analysed products (one vinegar and brown sugar), there were no significant statistical differences between the mean values provided by the two methods, if a confidence interval of 90% is to be considered as reference. For four of the analysed products (apple cider Elderflower, brown sugar and the two vinegars), there were no significant statistical differences between the mean values provided by the two methods, if a confidence interval of 98% is to be considered. For apple cider Golden apple and apple cider Redberries, statistical differences were recorded between the means of the two methods, at confidence levels inferior to 99.8%.

Table 2: The results of the t-test performed on the concentration values furnished by voltammetry and titrimetry.

Analysed product	$t_{calculated}$	Confidence level (%)	α value	$t_{tabulated}$
Apple cider Elderflower	2.752	98.0	0.020	2.896
Apple cider Golden apple	4.369	99.8	0.002	4.501
Apple cider Redberries	3.851	99.8	0.002	4.501
Vinegar (origin Greece)	1.616	90.0	0.100	1.860
Vinegar (origin Romania)	2.271	95.0	0.050	2.306
Brown sugar (origin Mauritius)	1.440	90.0	0.100	1.860

3.4 Polyphenol interference study

To provide information about the influence of matrix components, total polyphenol content (TPC) was analysed by the Folin-Ciocalteu method. The results in gallic acid equivalents (GAE) can be classified as follows - apple cider golden apple: 106 mg GAE /L; apple cider elderflower: 123 mg GAE /L, apple cider redberries: 210 mg GAE /L. This leads to a maximum of a 1:1 gravimetric ratio TPC/ sulfite, as per reference to sulfite results furnished by voltammetry (Na_2SO_3 mg L^{-1}).

Moreover, the voltammetric study performed on standard solutions showed that gallic acid perturbs the analytical voltammogram of sulfite at 1:1 (gallic acid/ sulfite) gravimetric ratio, determining a 30.4 % increase of the analytical signal.

Nevertheless, when analyzing ciders, the sulfite analytical signal led to a cyclic voltammetric result consistent with that provided by titrimetry (with less than 6% deviation between the two methods), and is confirmed by standard addition. Here, it should be added that Folin-Ciocalteu assay can be prone to interferences [36] from a series of compounds such as sulfur dioxide itself, but also sugars, organic acids, all being present in the analysed ciders. The analysed products contain, beside sulfite, malic acid, whose content was reported to increase during apple juice fermentation [37] and glucose-fructose syrup. Hence, the discrepancy may be explained by the fact that the values furnished by Folin - Ciocalteu method take account on the sum of the above-mentioned compounds and do not reflect only the TPC, because voltammetrically inactive compounds such as malic acid and sugars contribute to the analytical signal in Folin-Ciocalteu assay.

DuPont et al. [38] reported for cider a sum of phenolic compounds (cinnamic acid derivatives, benzoic acids, flavanols, flavonol-glycosides) of 48.19 mg L^{-1}, assessed by HPLC. Moreover, Ye et al. [37] obtained for apple juice, also by HPLC, a sum of phenolic compounds of 64.34 mg L^{-1}, with a decrease after fermentation that led to a 55.63 mg L^{-1} content in cider. Considering that the analysed beverages contain maximum 25% fermented apple juice, we may conclude that this leads to minimum interferences.

4 Conclusions

Several comparative and conclusive aspects can be inferred with respect to the applied analytical methodologies.

Both working Pt electrodes, measuring against different references, allow viable assay of sulfite, with confirmed analytical parameters and can be applied to quantifying this preservative from food and beverage samples.

The Pt strip electrode allows a larger linear range and a lower sensitivity (1.908 mg L^{-1} for Pt strip versus 3.168 mg L^{-1} for Pt ring), whereas the Pt ring electrode with Ag/AgCl reference incorporated is characterised by better repeatability, proven by a lower value of the relative standard deviation. Voltammetric determinations using both electrodes resulted in better precision than the photocolorimetric assay.

The sensitivity is greater for the Pt strip electrode Radelkis than for the Pt ring electrode Mettler-Toledo: 525.07 μA g^{-1} L for Pt strip vs 454.78 μA g^{-1} L for Pt ring, as proven by the slopes of the peak intensity dependences versus concentation. The same trend is observed for the slopes below 1 g L^{-1}: 695.99 μA g^{-1} L for Pt strip, compared to 599.79 μA g^{-1} L for Pt ring.

The linear range in photometry (10-80 mg L^{-1}) is less broad than that of voltammetry (15.5 mg L^{-1} – 4.0 g L^{-1} for the Pt ring electrode and to 7.5 mg L^{-1} – 4.0 g L^{-1} for the Pt strip electrode).

The results obtained by applying the voltammetric method to the assay of real samples, are correlatable to those furnished by the titrimetric method.

The beverages that contain significant amounts of reducing agents (such as phenolic antioxidants) cannot be analysed by the proposed techniques. We chose to analyse beverages that are not prone to interferences from phenolic compunds, such as: vinegars obtained from sugar fermentation (not from grapes or apple juice), sugar and commercial ciders containing maximum 25% apple juice.

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