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Pervaporation-Flow Injection Method for the Determination of Sulfur Dioxide in Food and Air Samples

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A pervaporation-flow injection method was developed for the analysis of sulfur dioxide (SO_2) in food and air samples. The method is based on the spectrophotometric measurement of the decrease in absorbance of malachite green (MG) solution at 617 nm due to pervaporated and subsequent dissolution of SO_2. The optimized system variables were MG concentration (2.4 x 10^{-5} M, buffered at pH 5.64 or 5.82), H_2SO_4 (0.20 M), donor stream flow rate (0.60 mL/min), acceptor stream flow rate (0.60 mL/min), reaction coil length from injector to donor chamber inlet (50.0 cm), reaction coil length from acceptor chamber outlet to flow cell (50.0 cm), and injection volume (60 µL). The optimized system has a linear working concentration range of 1-5 µg /mL SO_2 and the calculated limit of detection was 0.33±0.02 µg/mL SO_2 (7.6% RSD, n=4). The method was satisfactorily applied to the determination of SO_2 content of some wines, vinegar, beverage, and ambient air samples.

Key Words: flow injection, pervaporation, sulfites

INTRODUCTION

Sulfur dioxide (SO_2) is a major air pollutant since it is a combustion product of fossil fuels. It contributes to rainwater acidity and reduces atmospheric visibility. It is potentially toxic at high concentrations and in combination with particulates in the atmosphere. When SO_2 is dissolved in water, it forms the sulfite (SO_3^{2-}) ion.

Sulfites are mainly used to control microbial growth, bleach certain food starches, and prevent spoilage of certain perishable foods. Although generally recognized as safe, restriction on their use in food processing has become stringent in the U.S. and Europe because of reported adverse-allergic type reactions that were attributed to the consumption of foods containing sulfites which affect sulfite-sensitive asthmatics (http://www.allergies.com). Thus, to protect the consumers, the US government has required thru specific legislation, the sulfite warning label on all alcoholic beverages with at least 10 µg/mL SO_2.

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In the Philippines, the regulations and guidelines of the United Nation Food and Agricultural Organization/World Health Organization Codex Alimentarius Commission serve as reference points in determining food standards. Food processors in the country are advised to comply with these requirements of foreign buyers to be able to compete in the global market.

There are several analytical methods available for SO_2 analysis in food and air samples. Turbidimetry, colorimetry, and titration are among the traditional methods used (Lodge 1989; Greyson 1990). More recent techniques include chemiluminscence (Wu 1998), spectrophotometry (Lodge 1989; Sadegh 2003), capillary electrophoresis (Sadecka 1999), biosensor (Sezginturk 2005), ion chromatography (Wang 1999), and HPLC-UV (McFeeters 2003). Common drawbacks of these methods include time consuming procedures, expensive instrumentation, and the need to pretreat sample prior to detection.

The development of flow injection analysis (FIA) significantly contributed to the overcoming of these

drawbacks. Many of the above techniques were used as detectors in FIA, which incorporates sample pre-treatment and analysis (US FDA 1990). FIA methods for SO_2 in food and air samples can be classified into FIA with non-optical detectors (Corbo 2002, Chinvongamorn 2008) and FIA with optical detectors. The latter detectors include photometers (Ramasamy 1982), fluorometers (Mana 2001) and spectrophotometers (Mataix 1999, Melo 2003, Atanassov 2000).

The last four references cited analyzed wines for sulfite by transforming it to SO_2 gas. The SO_2 was separated from the sample matrix by diffusion through a membrane. The studies of Mana 2001, Melo 2003 and Atanassov 2000 used the gas diffusion-FIA technique, while the Mataix 1999 study used the pervaporation-FIA technique.

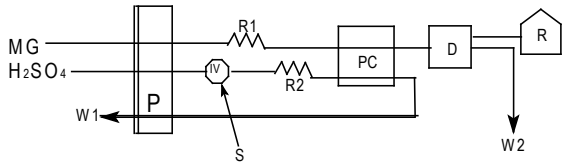
Pervaporation-Flow Injection Analysis (FIA) System

In this particular study, an integrated pervaporation-flow injection method was developed to determine SO_2 in food and air samples. Pervaporation (Mattos 1994; Bryce 1996) can be defined as a separation technique which combines continuous evaporation and gas diffusion through a gas permeable membrane which take place in the same unit. The volatile analyte or its volatile reaction product evaporates from the solid or liquid sample matrix to a space between the sample and the membrane. The analyte then diffuses through a membrane to a static or flowing acceptor stream. The development of pervaporation-flow injection methods requires relatively inexpensive instrumentation. It is expected that the proposed method would simplify SO_2 analysis due to low procedural cost and energy efficiency.

Sulfite has been previously quantified using conventional visible spectrophotometry (Safavi and Ensafi 1991) where the decrease in absorbance of an indicator dye (Brilliant Green) upon reaction with sulfite was measured and related to SO_2 concentration. The chemistry involved in this method was then adapted in the development of the proposed pervaporation-flow injection method.

The pervaporation-FIA system proposed manifold design is shown in Figure 1. The sample is injected into an acidic donor stream (H_2SO_4) where the SO_3^{-2} form is quantitatively converted to SO_2: $SO_3^{2-} + 2H^+ \rightarrow H_2O + SO_2$.

Sulfur dioxide evaporates and diffuses through the pervaporation membrane and dissolves in the flowing acceptor stream which contains the indicator dye solution. Malachite green (MG), a basic dye (Basic Green 4, triphenylmethane dye), reacts with the dissolved SO_2 which decreases the pH and absorbance of the dye solution. The decrease in the absorbance of the acceptor solution is monitored by a UV-vis spectrophotometric detector and transient signals are recorded.



IV = INJECTION VALVE
P = PERISTALTIC PUMP
PC= PERVAPORATION CELL
S = SAMPLE
W1,W2 = WASTES
R1,R2 = REACTION COILS
D = DETECTOR
R = RECORDER

Figure 1. Schematic diagram of pervaporation-flow injection manifold for spectrophotometric determination of SO_2 by Malachite Green Method.

This study differs from previous studies found by the authors in the literature, on the following counts:

(1) Pervaporation was used instead of gas diffusion. These two procedures give the advantage of separating the analyte, SO_2, from the sample matrix before going to the detector. Hence, tha analysis is unaffected by sample matrix parameters such as pH, suspended solids, conductivity and interferences like phosphate, nitrate and arsenate. The SO_2 separation from the sample matrix occurs by diffusion through a membrane. In gas diffusion, the membrane is in contact with the sample stream on one side, and with the acceptor stream on the other side. In pervaporation, as mentioned previously, there is a space between the sample and the membrane. Hence, there is no direct contact between sample matrix and the membrane that may cause clogging, contamination and deterioration of the membrane. This often happens in gas diffusion with red wines due to the presence of particulates (Mataix 1999).

(2) Malachite green (MG) reagent was used to react with the analyte SO_2. Other studies have used this reagent in non-FIA methods (Safavi and Ensafi 1991). The only study found by the authors in the literature, which used FIA-pervaporation for SO_2, was done by Mataix and de Castro in 1999. However, the reagents the Mataix study used (to react with SO_2) was para-rosaniline (PRA) and formaldehyde. In their respective MSDS's, PRA is a carcinogen and formaldehyde is a suspected carcinogen. The MSDS of MG states only that it is an irritant when swallowed.

(3) For SO_2 in air, previous studies on passive air samples

used analysis by ion chromatography, which requires expensive instrumentation. This study uses the simpler and cheaper optical method which can even be adapted to fabricated colorimeters in rural institutions which have no spectrophotometers.

MATERIALS AND METHODS

Reagents and Solutions

All chemicals used were of analytical reagent grade. Deionized water was used throughout. Degassing of solutions was done with a sonicator (NEY Ultrasonic Model 104H). Degassing removes dissolved gases in solutions and prevents formation of air bubbles in the flow channels of the system.

Sodium sulfite (Na_2SO_3): A 1,000 µg/mL primary stock solution (containing ~ 508 µg/mL SO_2) was prepared fresh every time from the reagent (Mallinkrodt, 99.0%). 100 µg/mL stock solution was prepared from the 1000 µg/mL primary stock. The various working standard solutions which range from 1 µg/mL to 10 µg/mL were prepared from the 100 µg/mL solution. Degassed deionized water was used in all preparations.

Sulfuric acid (H_2SO_4): A 4.0 M stock solution was prepared from the concentrated solution (Merck, 95-97%). More dilute acid solutions (0.05 M to .35 M) were prepared from the 4.0 M soln. The solutions were degassed immediately prior to their use.

Malachite Green (MG): A 5.0 X 10^{-4} M primary stock solution of this dye was prepared from the reagent (BDH, CI 42000, 90% w/w). More dilute solutions with absorbance readings ranging from 0.1 to 1.8 (ca 2.0 X 10^{-6} M to 2.0 X 10^{-5} M MG solutions) were prepared from the primary stock solution. The solutions were degassed immediately prior to their use.

Sodium hydroxide (NaOH): A 1.0 M primary stock solution was prepared from the pellets (J.T Baker, 99%). More dilute solutions (0.01 M to 0.1 M) were prepared from the 1.0 M stock solution.

UV-VIS spectra of the malachite green solutions for determining the optimum wavelength, slit width, and pH of solutions were measured in a 1.00 cm quartz cells using a Shimadzu UV-VIS-NIR Scanning Spectrophotometer (Model 3101PC) with a data station (AOC Computer System and Epson LX-800 Printer).

Pervaporation-FIA System

The pervaporation-FIA system was set-up following the proposed manifold design shown in Figure 1. System optimization was done using a univariate approach. Three sets of variables were optimized: UV-vis detector settings (λ_{max}, slit width), chemical (malachite green concentration, H_2SO_4 concentration, pH), and pervaporation-FIA variables (donor stream flow rate, acceptor stream flow rate, reaction coils length and sample volume).

The Analytical Pervaporation-FIA System: The schematic diagram of the pervaporation cell shown in Figure 2 was built at the Center for Scientific Instrumentation, La Trobe University, Bundoora Campus, Melbourne, Victoria. It consisted of the following parts: a) a donor chamber (DC) – the lower compartment in which the sample containing the analyte was introduced by injection,, (b) an acceptor chamber – the upper compartment in which the acceptor solution was circulated for receiving the pervaporated analytes, and (c) a pervaporation PTFE membrane (sometimes with an inert teflon support). Between the

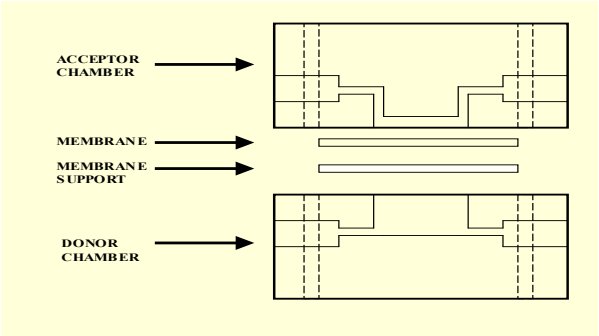


Figure 2. Schematic diagram of the Pervaporation cell.

flowing donor stream and the membrane was a constant air-gap which prevented contact between them. Clogging of the pores was greatly minimized. Both the chambers and membrane supports were aligned by means of two metallic rods and were clamped together using four-screws. The whole cell is made of perspex which permits continuous monitoring of the solution level in the donor chamber during the experiments.

A Perkin Elmer UV-VIS Spectrophotometer (Model Lamda 1) equipped with a QS Flow cell (10.0 mm path length) was used for the detection of the absorbance of the acceptor solution.

All manifold tubing used was made of PTFE (0.5 mm, Supelco).

The donor and acceptor streams were propelled by four-channel peristaltic pump (Watson Marlow) with variable flow-rate selector. Pump tubes with color codes black /

black and black/ white (Cole-Parmer) were used.

A Rheodyne six-way injection valve was used for sample introduction into the donor stream. Sample loops of varying volumes were attached to the injection valve one at a time.

Peak heights were recorded using a Shimadzu Chromatopac Integrator (Model CR6A).

Food Analysis

Liquid Samples

Different brands of liquid samples (wines, vinegars, and beverages) were bought from groceries and tested for their free SO_2 content. The samples were filtered and injected directly into the optimized pervaporation-FIA system. Sample free SO_2 concentrations were calculated using external standard calibration technique.

Ambient Air Analysis

Preparation of coating solutions for passive gas samplers: A 0.25 g NaOH was dissolved in 3 mL of 10 mM Mannitol. Mannitol was used to slow down sulfite oxidation to sulfate (DIONEX Application Note 54). The solution was diluted with methanol to 25 mL in a volumetric flask. The coating solutions were freshly made and air exposure was avoided. A 50µL of coating solution was pipetted evenly over the Whatman 40 filter paper.

The filter was mounted at the back of a short, wide tube; air was transported to the sorbent by molecular diffusion. In the open end of the tube, a stainless steel mesh acts as a wind and insect screen. A 1 uM Teflon filter was located behind the mesh to prevent aerosol from impacting onto the impregnated filter.

Sampling site selected was the area beside the Institute of Chemistry, UP Diliman building where chemical wastes are temporarily stored. A 1.5 m high wooden pole was installed at the site and a common plastic Frisbee screwed to the top. The Frisbee acted as a weather (rain) shield for the sampler. An aluminium channel was installed as a sampler holder. The sampler is removed from its container and an identifying code and time of deployment were recorded. The sampler was then installed mesh-side down in the channel on the underside of the Frisbee and left in position. Six samplers were exposed for a month. Two sampling periods were done: from August-September, 2005 and September to October, 2005.

After exposure of passive samplers, SO_2 trapped as sulfite in the filter paper was extracted in a glass vial by addition of 4 mL ultrapure water. The solution was sonicated for 15 min, filtered, and injected into the optimized pervaporation-FIA system. The SO_2 concentration was calculated using external standard calibration technique and ppbV SO_2 in air was calculated using equation 1 (Sadegh et al. 2003):

$$\text{ppbV } SO_2 = \{L \times EV \times [SO_2] / (T \times DC)\} \times 0.382^* \quad \text{Equation 1}$$

where: L = total air resistance, 41.2 m^{-1}
EV = extraction volume in mL
$[SO_2]$ = ug/mL (from calibration graph)
T = sampling time in seconds
DC = diffusion coefficient = 1.32×10^{-5} m^2/s for SO_2

* at 25°C, 0.382 ppbV SO_2 = 1 µg/m^3 (14).

Validation Methods

The obtained results from the pervaporation-flow injection method were compared with the results obtained using another standard or reference method. Iodimetric titration method was used as reference method for the analysis of free SO_2 in vinegar, wines, and beverage samples. Sulfite is titrated with an iodide-iodate solution using a starch end point indicator.

For the analysis of the air samples, ion chromatography was used as the reference method. After exposure of passive samplers, SO_2 trapped as sulfite in the filter was extracted with 1.5 mL of 1.0×10^{-2} M H_2O_2 solution and sonicated for 15 minutes to ensure complete oxidation to sulfate prior to injection into the ion chromatograph. The sulfate concentration (expressed as µg/mL SO_2) was calculated using external standard calibration technique and ppbV SO_2 in air was calculated using equation 1. Statistical test (i.e., t-test) was conducted to determine the presence or absence of systematic error in the pervaporation-FIA method.

RESULTS AND DISCUSSION

Optimization of Experimental Variables

The variables of the system were split into three areas: UV-vis detector settings, chemical variables, and pervaporation-FIA variables. The variables were optimized using the univariate method.

The optimum wavelength chosen for the determination of sulfite based on malachite green was 617.0 nm, the wavelength at which the largest detectable decrease in MG absorbance was recorded when sulfite was introduced. Data showing the effect of added SO_2 on the absorbance of malachite green at different wavelengths tested is shown in Table 1.

Relatively higher absorbance readings were obtained for slit widths in the range 1.0 – 3.0 nm. For the actual

Table 1. The effect of added SO_2 on 2.4 x 10^{-5}M MG absorbance at different wavelengths.

SO_2added (µg/mL)	Δ Abs			
	617 nm	423 nm	316 nm	253 nm
Ao (initial)	1.1781	0.2559	0.2600	0.2596
1.00	0.1423	0.0300	0.0246	0.0228
2.00	0.0917	0.0190	0.0176	0.0061
3.00	0.0106	0.0009	0.0027	-0.0376
4.00	0.0048	0.0026	0.0016	0.0424
5.00	0.0576	0.0122	0.0126	-0.0316
6.00	0.0022	0.0002	0.0002	0.0127
7.00	0.0697	0.0151	0.0125	0.0220

Table 2. The effect on the absorbance of 2.4 x 10^{-5} M MG at λ = 617.0 nm with varying H_2SO_4 concentration when 10 ug/mL SO_2 is added.

	Decrease in MG Absorbance x 100			
	Number of Trials			
H_2SO_4, M	1	2	3	Average
0.05	27	27	28	27.3
0.10	33	35	35	34.3
0.15	35	34	35	34.7
0.20	41	41	44	42.0
0.25	40	41	41	40.7
0.30	37	36	38	37.0
0.35	34	37	35	35.3

determinations, 2.0 nm slit width was used although 1.0 nm and 3.0 nm could also be used.

The effect on the absorbance of 2.4 x 10 $^{-5}$ M MG (A~ 1.178) solution with varying concentration of H_2SO_4 (0.05-0.35 M) when 10 ug/mL SO_2 solution is added is shown in Table 2. The concentration of the H_2SO_4 acid influences the acidity for sulfite liberation. The results showed that a H_2SO_4 concentration of 0.20 M gave the largest % decrease in the MG absorbance and was therefore considered as the optimum concentration of H_2SO_4 for sulfite liberation.

Malachite green concentration and pH are very important variables since these define the baseline of the recorded fiagrams. Figure 3 shows a plot of 4.0 x 10^{-5} M MG absorbance as a function of pH. Maximum absorbance was obtained at pH 5.64 -5.82. Because of the relatively noisy signals observed for the higher concentrations of

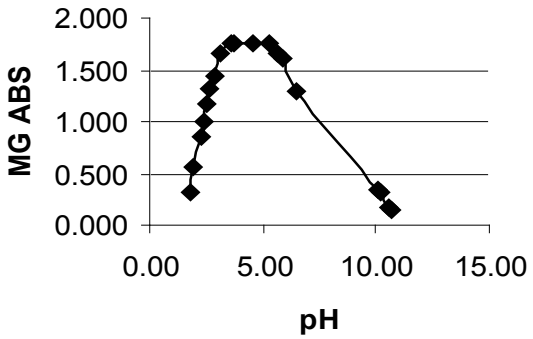


Figure 3. Change in the absorbance of Malachite Green as a function of pH.
λ = 617 nm. 4.0 x 10-5 M MG prepared in distilled water.

Table 3. Pervaporation-Flow Injection Analysis Parameters.

Parameter	Range studied	Optimum value
Flow rate, MG soln (acceptor stream)	0.5 – 2.0 mL / min	0.6 mL / min
Flow rate, H_2SO_4 soln (donor stream)	0.50 – 2.0 mL / min	0.6 mL / min
Reaction coil length, acceptor outlet to flow cell	25 – 120 cm	50.0 cm
Reaction coil length, injector to donor inlet	25 – 120 cm	50.0 cm
Sample volume	20 - 500 µ L	60 µ L

MG, the solution with the approximate concentration of 2.4 X 10^{-5} M (A ~ 1.0) was chosen which showed less noise but still gave appreciable signal. Improved measurement conditions were attained at 2.4 x 10^{-5} M malachite green solution buffered at pH 5.64 or pH 5.82.

The results of the optimization of the pervaporation-FIA parameters are shown in Table 3. The parameters were optimized using a univariate approach. The optimum parameter value taken was the one that gave the largest FIA signal (recorded as peak height). The best performance of the system was achieved when both the donor stream and acceptor stream are propelled at the same flow rate which is at 0.6 mL/min and the two reaction coils are of the same length (50.0 cm). A compromise was adopted between low and high flow rates. Long sample residence time in the donor chamber and efficient mass transfer was achieved at low flow rates but this resulted in high sample dispersion during the transport of the reaction product from the acceptor chamber to the detector. On the other hand, short sample residence time and less efficient mass transfer and low sample dispersion occurred at high flow rates.

Characterization of the optimized pervaporation-

Table 4. Standard calibration studies on the optimized pervaporation-Flow Injection Analysis system.

Trials	Concentration range, µg/mL SO_2	Equation of line	R^2	LOD, µg/mL	Sensitivity, ΔPH,mm/µg/mL
Set A1	1-5	y = 11.84x + 1.70	0.9993	0.30	11.84
A2	1-5	y = 10.84x + 4.69	0.9848	0.33	10.84
A3	1-5	y = 9.95x + 1.35	0.9912	0.36	9.95
A4	1-5	y = 11.00x + 5.20	0.9856	0.32	11.00
Set B1	2-10	y = 11.88x – 14.60	0.9603	0.42	11.88
B2	2-10	y = 9.14x + 23.68	0.9338	0.39	9.14
B3	2-10	y = 6.64x + 0.24	0.9805	0.54	6.64

FIA system using standard solutions of SO_2

The response of the pervaporation-FIA system was calibrated repeatedly at various times using standard solutions of SO_2 and at the optimum working conditions. The results of such study are shown in Table 4.

Two sets of working SO_2 standards were used in the calibration, 1-5 µg/mL (Set A) and 2-10 µg/mL (Set B). The limit of detection (LOD) was calculated using the equation LOD = 3σ blank/m, slope of standard calibration curve. Better linearity, higher calibration sensitivity, lower detection limits, and better precision were achieved at the concentration range 1-5 ug/mL. For the concentration range 1-5 µg/mL SO_2, an average LOD of 0.33 ± 0.02 µg/mL (7.6% RSD, n=4) was calculated while for 2-10 µg/mL SO_2, the calculated average LOD was 0.45 0.08 µg/mL SO_2 (17.6% RSD, n=3). The linear regression coefficient, R^2, of standard calibration plot for the concentration range 1-5 µg/mL varies from 0.9848 – 0.9993, while for the concentration range 2-10 µg/mL varies from 0.9338 – 0.9805. The calibration sensitivity, m, for the concentration range 1-5 µg/mL SO_2 was found to be equal to 10.91 ± 0.77 (7.10% RSD for n=4) and for the concentration range 2-10 µg/mL, was found to be equal to 9.22± 2.62 (28.43 % RSD for n=3). From these results, we can conclude that the optimized pervaporation-FIA system is best applied to samples with low concentrations of SO_2 (< 5 ug/mL). However, concentrations greater than 5 ug/mL can still be analyzed by diluting the sample within the optimum linear working concentration range of the system.

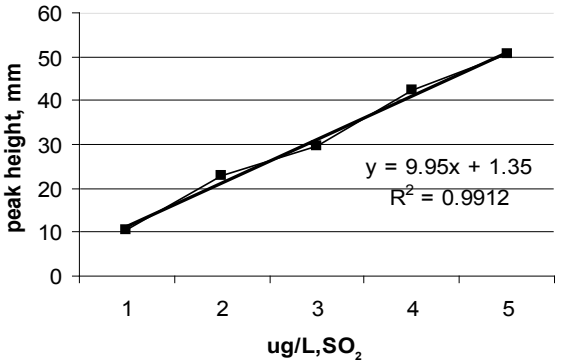


Figure 4. Typical standard calibration plots obtained by injecting 1-5 µg/mL SO_2 solutions into the optimized Pervaporation-FIA system.

Application of the optimized pervaporation-FIA method to the analysis of beverage and vinegar samples and air samples

Analysis of free SO_2 in vinegar and beverage samples

The optimized pervaporation-FIA method was applied to the analysis of free sulfite (as µg/mL SO_2) in vinegar and beverage samples. The results are shown in Table 5 for n=3. It can be seen in Table 5 that the precision of the proposed method ranges from 8.5 %-27% RSD depending on the type of sample. To validate the method and demonstrate its usefulness, and also taking into account the lack of certified reference materials for this analyte, the free SO_2 content of the same samples were determined by iodimetric method. The titrimetric iodimetric method (reference method) is based on the "Ripper" method which has been used for years by the wine industry as a standard for rapid sulfite analysis. Sulfite is titrated with an iodide-iodate solution using a starch end point indicator. The method determines free sulfite as µg/mL SO_2 and is the recommended method by the European Community (EU). The results of the titrimetric analysis of the same samples are also shown in Table 5 for n=3. It can be seen that the precision of the reference method ranges from 7.2% – 43% RSD depending on type of sample.

The mean value $\overline{X}$ from the analysis of the proposed method (pervaporation-FIA method) was compared with the mean value $\overline{X}$ of the reference method (Titrimetric method) using the t-test at 95% C.L. If the observed

Table 5. Free SO_2 contents in vinegar and beverage samples as determined by pervaporation-FIA method (proposed method) and Iodimetric method (reference method).

Sample	Pervaporation-FIA µg/mL SO_2 (n=3)	Iodimetric method µg/mL SO_2(n=3)	t-test at 95% C.L. $t_{95\%}$ = 2.78 at n=4
Boone's white wine	2.44 ± 0.66	2.38 ± 0.44	0.13<2.78
Carlos rossi white wine	17.01 ± 1.44	18.26 ± 1.32	1.11<2.78
UFC vinegar	7.60 ± 1.15	7.37 ± 3.19	0.12<2.78
Silver swan vinegar	0.89 ± 0.19	0.69 ± 0.28	1.02<2.78
Zesto lemon soda	3.14 ± 0.51	2.76 ± 0	1.29<2.78
Datu puti vinegar	2.53 ± 0.36	2.07 ± 0.53	2.49<2.78
Filtaste	4.42 ± 0.48	4.15 ± 1.60	0.28<2.78

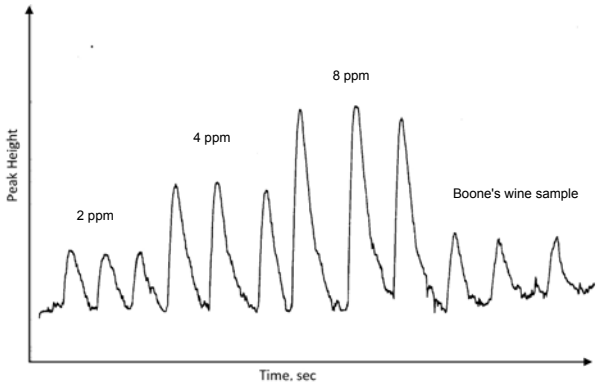


Figure 5. Typical pervaporation-FIA responses of standards and wine sample at optimum experimental conditions.

difference between the means is less than that computed at 95% C.L., the null hypothesis that the two means are the same cannot be rejected and no systematic error has been demonstrated. The results of t-test are shown in Table 5. Based on the t-test, the proposed method results are not significantly different ($t_{calc}<t_{95\%}$) from the reference method. Figure 5 shows a typical FIAgram of standards and wine sample. The sample throughput of this method is estimated at a maximum of 12 samples per hour.

Analysis of SO_2 in ambient air

Passive samplers are devices that are able to fix either gaseous compounds or vapours from the atmosphere without involving active air movement through the sampler. The gas to be measured is trapped on a filter impregnated with a water-soluble substance. After exposure, the gas is extracted from the filter and analyzed usually by ion chromatography if gas is SO_2.

The SO_2 content of passive gas samplers after a month exposure at the chosen site (beside the Institute of Chemistry building where chemical wastes are temporarily stored) were determined using the developed pervaporation-FIA method and compared with the ion-chromatography method. The results are shown in Table 6. Based on the t-test, the pervaporation-FIA method results are not significantly different ($t_{calc} < t_{95\%}$) from the ion-chromatographic method. The precision of the developed method (6-17% RSD) were also comparable with the ion-chromatographic method (6-9% RSD). The results suggests that passive SO_2 sampling with pervaporation FIA detection could be a simple and low-cost alternative method for monitoring atmospheric SO_2 concentration compared to passive sampling and ion-chromatography detection. The standard DENR method for analysis of SO_2 in air is colorimetric determination with pararosaniline (Dasgupta et al. 1980), a triaminotriphenylmethane dye which is reported mutagenic and carcinogenic in its MSDS (Material Safety Data Sheet). Malachite Green, the dye used in this study, has no known carcinogenic effects and is stated in its MSDS as only harmful (may cause irritation) if swallowed.

Table 6. Comparative Results: Total SO_2 in passive gas samplers as determined by pervaporation-FIA method (proposed method) and Ion chromatography (reference method).

Passive SO_2 samplers	Pervaporation-FIA ppbV SO_2 (n=3)	Ion chromatography ppbV SO_2 (n=3)	t-test at 95% C.L. $t_{95\%}$ = 2.78 at n=4
August'05-September'05 sampling	2.60±0.45	3.10±0.18	1.78<2.78
September'05-October'05 sampling	2.04±0.12	1.79±0.16	1.83<2.78

CONCLUSIONS

The developed pervaporation-FIA method for SO_2 determination in liquid food samples and ambient air samples have been shown to yield results in agreement with those obtained by alternative procedures such as iodimetric and ion-chromatography methods. The calculated limit of detection of the method is 0.33 ± 0.02 µg/mL SO_2, and is therefore applicable to trace determinations of sulfite/sulfur dioxide. The system can handle approximately 12 samples per hour yielding precise results. Only 60 µL of sample and approximately 3 mL each of MG and H_2SO_4 solution are required per determination. The pervaporation –FIA method using MG for SO_2 in food and air samples can be a simple, interference-free and low-cost alternative method in place of iodometric and ion-chromatography methods. In addition, dramatically less amounts of chemicals are consumed plus a much less toxic dye (MG) is used in comparison with PRA, which was used in previous studies and is also used in the standard DENR method for analysis of SO_2 in air.

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