



Flow injection analysis–flame atomic absorption spectrometry system for indirect determination of sulfite after on-line reduction of solid-phase manganese (IV) dioxide reactor

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ABSTRACT

A new and simple flow injection method followed by atomic absorption spectrometry was developed for indirect determination of sulfite. The proposed method is based on the oxidation of sulfite to sulphate ion using solid-phase manganese dioxide (30% W/W suspended on silica gel beads) reactor. MnO_2 will be reduced to Mn(II) by sample injection in to the column under acidic carrier stream of HNO_3 (pH 2) with flow rate of 3.5 mL min^{-1} at room temperature. Absorption measurement of Mn(II) which is proportional to the concentration of sulfite in the sample was carried out by atomic absorption spectrometry. The calibration curve was linear up to 25 mg L^{-1} with a detection limit (DL) of 0.08 mg L^{-1} for $400 \mu\text{L}$ injection sample volume. The presented method is efficient toward sulfite determination in sugar and water samples with a relative standard deviation (RSD) less than 1.2% and a sampling rate of about 60 h^{-1} .

1. Introduction

Sulfite or sulphite is widely used as an additive in foods and beverages in order to prevent oxidation, bacterial growth and to control enzymatic reactions during the production and storage processes. As it has been used in these products, adverse health effects of sulfite are well documented: when consumption above permissible limit (set by the US Food and Drug Administration), sulfite poses a great danger by causing nasal congestion, coughing, breathing difficulties, asthma, itching, hives and other skin rashes. It also causes headache, abdominal pain, diarrhea resulting in fatigue and irritation. The mentioned symptoms occur quickly within 20–30 min after consuming sulfite-containing food stuff such as bottled canned or frozen fruits, baked foods, beer and wine [1].

Sulfite is an analyte of special interest for environmental control and food processing because it acts as a parameter indicating acid rain (5.0 mg m^{-3} of sulfite in Air at 15°C gives $\text{pH} = 4.6$) and stabilization, respectively. In the latter case, it is used to inhibit the growth of moulds, yeast and aerobic bacteria, and to prevent the darkening of fruits, soups, fruit juices, beer and wine. However, sulfite causes attacks of asthma in some individuals, and occasionally death. Since a suitable replacement additive has not been found, sulfite is still used in wine and some other processed foods. For the purpose of regulation, the amount

present is calculated like sulphur dioxide gas [2].

Various technologies including titration [1–5], flow-injection amperometry detection [6–9], spectrophotometry [10,11], spectrofluorimetry [12–20], flow-injection analysis–chemiluminescence (FIA-CL) [21], flame atomic absorption spectrometry (FAAS) [22], ion chromatography (IC) [23–26], liquid chromatography–mass spectrometry (LC-MS) [27], high-performance liquid chromatography (HPLC) [28], electrochemical methods [29–36] and fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) [37] have been employed for determination of sulfites.

Up to now, there have been a few investigations about solid-phase reactors and their applications in determination of inorganic and organic compounds. Recently, by incorporating the solid-phase reactors in to flow injection analysis (FIA) manifolds numerous advantages will be attained over homogeneous systems such as low consumption of reagents and organic solvents, in situ preparation of unstable reagents and also simple operation with fewer junctions in mixing of reagents, sample and carrier streams [38–43].

The interaction of oxidizable organic and inorganic compounds with soil MnO_2 mineral by spectroscopic techniques has received a little attention [44–47]. Mn quantities in soils and geochemical sediments are generally assumed to be mediated by redox reactions. The data based on frontier molecular orbital theory (FMOT) considerations show

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that oxidating compounds like Mn(IV) can oxidize organic compounds faster than dioxygen ones [45]. Manganese dioxide has been applied to oxidation of Cr(III) [46,47], catechol [45], alcohols [44], and aniline [48]. In all studies, manganese dioxides are reduced to Mn(II). To the best of our knowledge, no manganese dioxide based solid-phase reactor has been utilized for an analytical determination. According to our basic studies, sulfite can reduce MnO₂ to Mn(II) under acidic media.

In this study a manganese dioxide based solid-phase reactor was developed for the first time and applied for automatic indirect determination of sulfite by AAS detection method without using any other separation techniques.

2. Material and methods

2.1. Reagents and solutions

All reagents were prepared from analytical reagent grade chemicals unless specified otherwise. All aqueous solutions were prepared with redistilled water. Before each measurement, sulfite stock solution 500 mg L⁻¹ was prepared freshly by dissolving 0.0825 g of sodium sulfite in 100 mL water. The solution for the carrier stream with pH 2, was prepared by dilution of HNO₃ (Merck Co., Germany) with redistilled water to a final concentration of 6.3 mM. Before mixing with manganese dioxide (Merck Co., Germany), the silica gel beads (mesh 230–400, 0.04–0.063 mm; Merck Co., Germany) were treated at 950 °C for three hours in order to dehydrate irreversibly [49].

2.2. Instrumentation

Schematic diagram of a typical flow injection system is given in Fig. 1. A variable flow-rate liquid chromatography pump (Bruker, Germany, Model LC22) was used to pump carrier-streams and sample through the manifold at a flow rate of 3.5 mL min⁻¹ via a degasser (Erma, Tokyo, Model ERC-3522). The manifold lines consisted of 0.8 mm i.d. polyethylene tubing. The six-way injection valve (Rheodyne, USA, Model 7125) allowed the sample to be directly loaded in to a 400 µL loop, and subsequently injected into the carrier stream. The injection valve was kept in the load position for the first 10 s of every run to load the sample loop. After, it was switched to the inject position to place the sample plug in to the carrier stream. The valve was kept in the inject position for a further 30 s to ensure that the entire sample was flushed out of the sample loop. This was followed by switching the valve to the load position to fill the sample loop for the next run. After being placed in the carrier stream, the sample zone was pumped through the solid-phase reactor. The products were channeled to a flame atomic absorption spectrometer (Philips, Model PU 9110X) with an air-acetylene flame and 5 cm optical path-length (burner). The light source was a Mn hollow cathode lamp. The wavelength was set to 279.5 nm with a spectral slit-width of 0.5 nm and a lamp current of 12 mA. A pH-meter (632, Metrohm, Switzerland) with a Metrohm double junction glass electrode was used for monitoring pH adjustment.

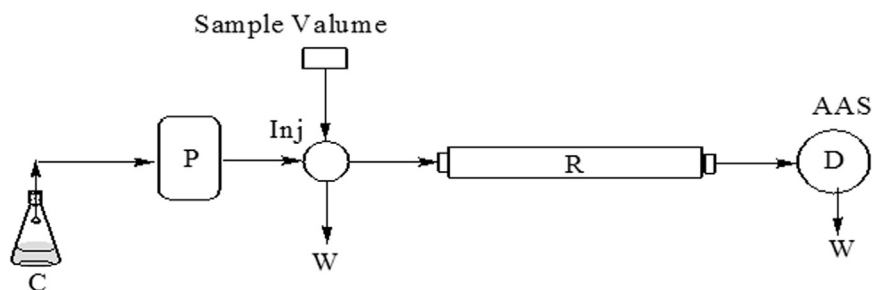


Fig. 1. Schematic diagram of the single-line flow injection system used for determination of sulfite. C, carrier; P, pump; Inj, injector loop valve; R, solid-phase reactor; D, detector; W, waste.

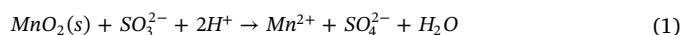
2.3. The solid-phase reactor

The solid-phase reactor was constructed from stainless-steel tubing with i.d. of 3 mm and length 100 mm. The tubing was packed by silica gel beads embedded in solid MnO₂. The reactor was prepared by mixing 0.7 g powdered solid manganese dioxide (Merck) and 1.4 g of silica gel beads. The mixture was homogenated using an IR vibration mill (Shimadzu, Japan). Each packed reactor should be conditioned for at least 40 min before use. Conditioning process involved pumping redistilled water through the reactor for 20 min followed by pumping carrier stream, 6.3 mM HNO₃ (pH 2), for another 20 min at a flow rate of 3.5 mL min⁻¹. For each reactor, the lifetime was established by comparing absorbance with the same standard from day to day. When the absorbance started to be decrease systematically the reactor had to be replaced by the new one.

3. Results and discussion

3.1. Analysis with MnO₂

As reported in previous studies [44–47], the equation for describing the net reaction between a compound (sulfite in this work) and MnO₂ under acidic condition is as follows (Eq. (1)):



As could be seen, sulfite (SO₃²⁻) reduces MnO₂ to Mn(II) and sulphate (SO₄²⁻) is formed. On the other hand, Mn(II) absorbance is proportional to the concentration of sulfite in the sample. Hence, manganese dioxide can be regarded as a reagent for determination of sulfite in flow injection system. According to the Eq. (1) which indicates the basis for sulfite determination, by addition an excess amount of sulfite in to the reaction more MnO₂ is consumed and more Mn(II) ions is achieved consequently.

3.2. Optimization of variables

The performance of the proposed flow-injection system depends on the efficiency of the reaction between the solid and liquid phases of the reactor. In this way the effect of main factors such as HNO₃ concentration in carrier stream, MnO₂ concentration in reagent section, loop volume and the temperature should be optimized. Contact time is another important parameter required to be optimized in order to improve the interaction between zone containing sulfite and the reactor sufficiently. In this regard, the flow rate of the carrier stream through the reactor was utilized in the range of 0.5–8.0 mL min⁻¹. The effect of carrier flow rate on the final response is shown in Fig. 2. The highest analytical signal (Absorbance) was found at the rate of 3.5 mL min⁻¹. At the flow rates lower than 3.5 mL min⁻¹, the resulting absorbance is become down, due to the increased longitudinal diffusion. As a result of uncompleted reaction between sulfite and MnO₂, a decrease in absorbance was also found at flow rates above 3.5 mL min⁻¹. According to these results the carrier flow rate of 3.5 mL min⁻¹ was selected to obtain maximum sensitivity and minimum residence times. By this way at least 60 injections per hour can be performed.

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