

Determination Of Sulfite In Food

Purpose

Determination of sulfite concentrations in a variety of consumables. Sulfite determination has become increasingly important in the U.S. as pressure grows to ban sulfite as a food and pharmaceutical additive. Sulfite is added primarily as a preservative, frequently to fresh vegetables during transport and display (e.g. salad bars, market displays) as well as to preserved fruit and vegetable products. Sulfite is known to cause a severe allergic type of response in susceptible individuals. The U.S. Food and Drug Administration (FDA) requires that processed-food labels disclose the presence of sulfites whenever they are detectable in the finished products at ≥ 10 ppm.

Existing Methods

The classical Monier-Williams method, where sulfite is distilled from the food matrix. The procedure is time consuming and lacks sensitivity and specificity. Volatile compounds from certain foods interfere with sulfite determinations. Modified Monier-Williams distillation methods utilizing pulse polarography and square wave voltammetry have also been used. LC separation with electrochemical detection of free and

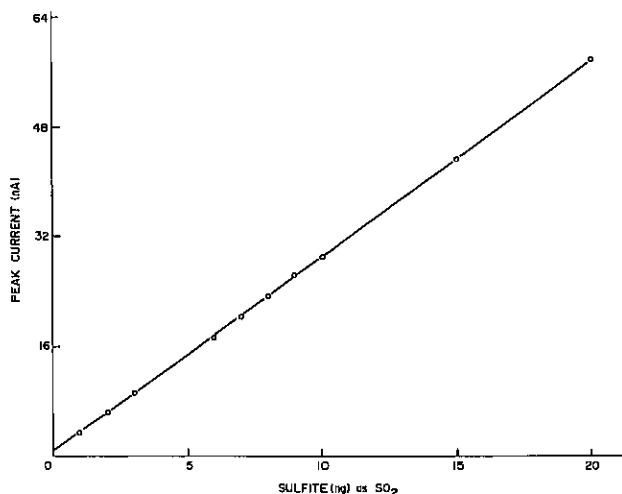


Figure 1. Calibration curve for sulfite. Volume injected was 5 μ L.

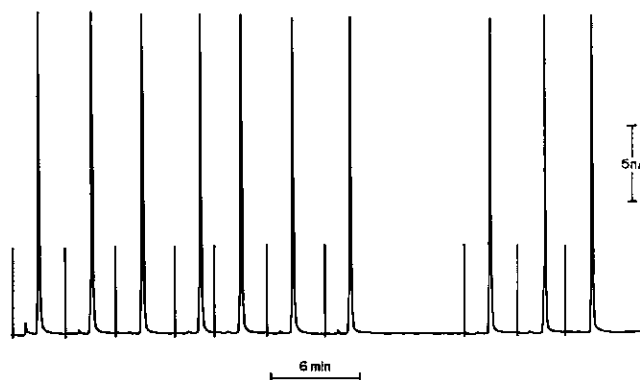


Figure 2. Reproducibility of sulfite response. Each injection contained 1 ng SO₂ in 5 μ L.

total sulfite has recently been pioneered by Kim et al.

LCEC Method

Offers a rapid, accurate, and sensitive alternative to the determination of free and bound sulfite in a variety of foods.

Conditions

System: BAS 200 or BAS 400.

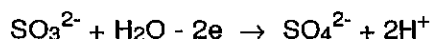
Column: Brownlee Polypore H ion exclusion column, 10 μ m, 100 x 4.6 mm.

Mobile Phase: 10 mM H₂SO₄ with 10 mM mannitol, deoxygenated by a 10 min. purge with helium. Flow rate was 0.5 mL/min.

Electrode: platinum (BAS, P/N MF-1012)

Potential: +700 mV vs Ag/AgCl.

Principle: At the applied potential sulfite is oxidized to sulfate:



Sample Preparation -- direct extraction

For solid samples, weigh out 0.1 - 1.0 g, add 10 - 100 mL of extraction solution and homogenize. The

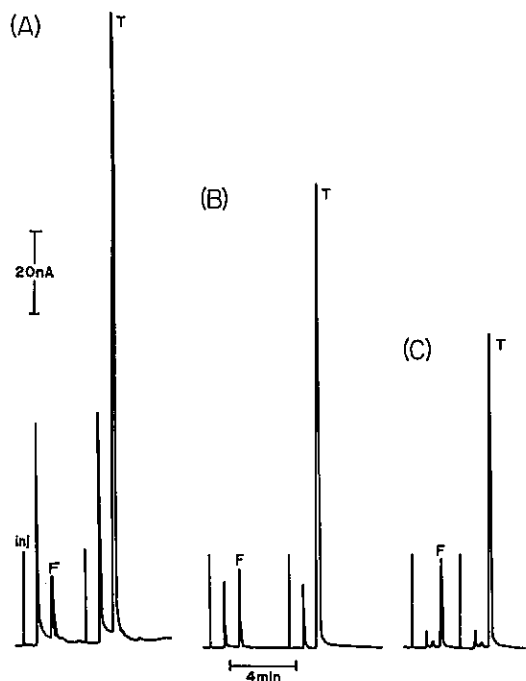


Figure 3. Chromatograms of food samples for free (F) and total (T) sulfite. A, white wine; B, lime juice; C, mashed potato powder. 5 µL of clarified solution injected.

extraction solution for free sulfite was composed of 5 mM H₂SO₄ (pH 2) and 10 mM D-mannitol, for total sulfite the composition was 20 mM Na₂HPO₄ (pH 8.9) and 10 mM D-mannitol. The extraction solutions were thoroughly purged with helium before use.

For liquid samples, such as lemon juice, dilute with 10 - 100 volumes of pH 2 or pH 8.9 extraction solution.

Centrifuge the homogenate or diluted liquid samples for 3 min. at 1600 x g to remove particulate matter. Filter the supernatant through a 0.45 µm microfilter (BAS P/N MF-5500), or pass it through an activated Sep-Pak cartridge (Millipore, Milford, MA, USA). Inject a 5 µL aliquot into the chromatograph (F2 and F3).

Detection Limit

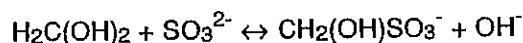
10 pg as SO₂ injected, at a S/N = 3. The injection volume was 5 µL which corresponds to a concentration of 2 ppb as SO₂ in the original solution.

Linear Range

0 to 10 ng injected, corresponding to concentrations of 0 to 2 ppm as SO₂ in liquid samples or 0 to 2 µg/g in a solid sample (F1).

Sample Preparation -- via adduct formation

In solution, pH 3-7, sulfite rapidly combines with formaldehyde to form hydroxymethanesulfonate (HMS):



This adduct (HMS) is very stable (at the pH used for extraction), thus protecting the sulfite from oxidation by other active materials found in complex food samples, for example enzymes. HMS is not detectable under the conditions employed above. Under alkaline conditions the above equilibrium is shifted to the left and the released sulfite can be determined under the present LCEC conditions.

Weight out 0.1 - 1.0 g of solid sample, add 10-100 mL of 0.07% formaldehyde solution (2 mL of 37% formaldehyde to 998 mL of 0.1 M sodium citrate adjusted to pH 5.1 with acetic acid) and homogenize. Centrifuge and filter, or pass through a Sep-Pak (see above). Mix 100 µL of the clarified homogenate with 900 µL of 0.1 N NaOH solution. Inject 5 µL into the chromatograph (F5).

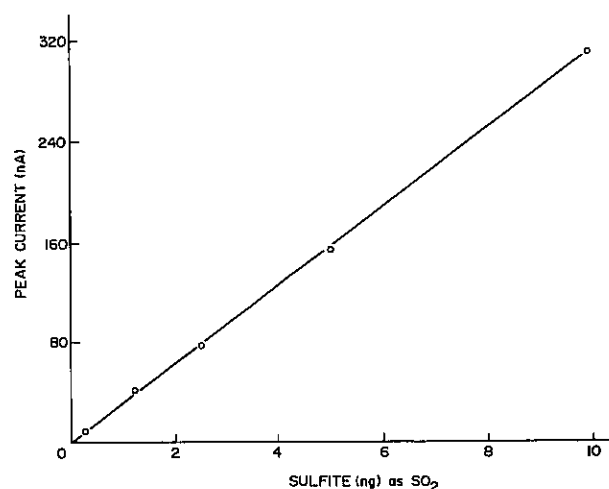


Figure 4. Calibration curve for sulfite via adduct formation. Volume injected was 5 µL.

Detection Limit

30 pg as SO₂ injected, at a S/N = 3. The injection volume was 5 µL which corresponds to a concentration of 6 ppb as SO₂ in the original solution.

Linear Range

0 to 20 ng injected, corresponding to concentrations of 0 to 4 ppm as SO₂ in liquid samples or 0 to 4 µg/g in a solid sample (F4).

Note

Pretreatment of the Pt-working electrode is critical to precision and linear response, contact BAS for details.

References

1. T. Huang, C.T. Duda, and P.T. Kissinger, *Current Separations* 8(1987) No. 3/4, 49 (BAS Press).
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3. H.-J. Kim and Y.-K. Kim, *J. Food Sci.*, 51(1986) 1360.
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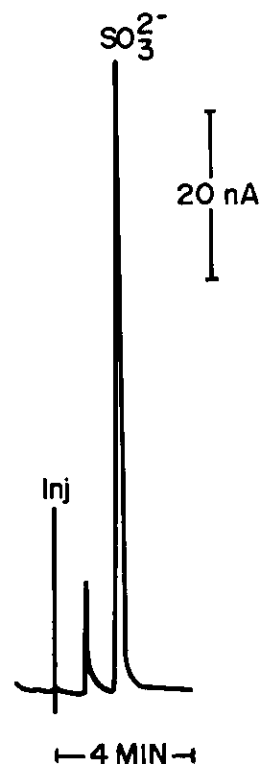


Figure 5. Chromatogram of total sulfite in dried mixed fruit - via adduct formation. 5 µL of clarified homogenate injected.