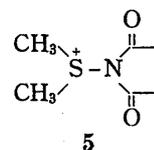


Among known methods for synthesis of triarylsulfonium ions,<sup>8-10)</sup> the simplest is the aluminum halides-catalyzed reaction of sulfoxide with benzene.<sup>8)</sup> Though the reaction conditions are drastic, the mechanism may be closely related to the present reaction. An example of a sulfonium ion postulated as an intermediate attacking arenes is dimethylsulfonium ion of type 5.<sup>11)</sup> However, the reagent reacts only with phenol, and the mechanism is preferably interpreted by an intramolecular rearrangement of a sulfonium ion formed by the attack of phenolic oxygen.<sup>12)</sup> From a synthetic stand-point, the reaction found here is the most promising method for synthesis of triarylsulfonium salts.



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### High Performance Liquid Chromatographic Analysis of Sulfite using Malachite Green

A selective, sensitive and accurate determination of sulfite was proposed by high performance liquid chromatography (HPLC). The sulfite was converted quantitatively to an adduct by reacting with a triphenylmethane dye, malachite green (MG). The formation of adduct was complete, and the adduct was stable at the experimental conditions. Then, the adduct was submitted to HPLC. The working curve for sulfite was linear in the range from  $2.0 \times 10^{-12}$  mol upto  $1.2 \times 10^{-9}$  mol.

**Keywords**—sulfite; triphenylmethane dye; malachite green; adduct formation; sulfite-malachite green adduct; high performance liquid chromatography

It is well known that sulfite taken into body from environment may have harmful effects on body for its easiness of interactions with various biological constituents.<sup>1)</sup> Therefore, it is significant to analyse sulfite exactly. However, analysis of sulfite is rather difficult, since sulfite is apt to be oxidised under aerobic conditions. There has been no report which refers to the method for highly sensitive and accurate determination of sulfite. Recently, ion chromatographic method has been reported by Small, Stevens and Bauman,<sup>2)</sup> but this method may not be reliable for the estimation of sulfite.

In the present communication, the authors describe analysis of sulfite (bisulfite) using a triphenylmethane (TPM) dye, malachite green (MG) as a ultra violet tagging pre-column reagent by high performance liquid chromatography (HPLC). It has been known that several TPM dyes react with both of sulfite and bisulfite to form decolored leuco-type adducts,<sup>3)</sup> and the reaction of *p*-rosaniline-sulfite adduct with formaldehyde has been applied to the colorimetric determination of sulfite in West-Gaeke method<sup>4)</sup> and other modified colorimetric method.<sup>5)</sup>

The adduct was formed easily by mixing the solution of a dye and that of sulfite (bisulfite). Among several TPM dyes examined, MG formed the adduct which had the strongest absorption

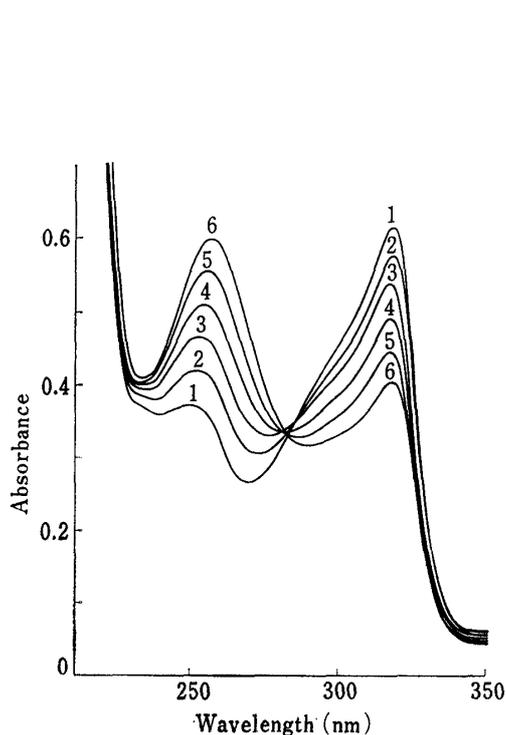


Fig. 1. Spectral Change of Malachite Green (MG) with Addition of Sulfite

Concentration of MG 1—6 :  $2 \times 10^{-5}$  M.  
 Concentration of sulfite ( $\times 10^{-5}$  M)  
 1 : 0, 2 : 0.4, 3 : 0.8, 4 : 1.2, 5 : 1.6, 6 : 2.0.  
 Buffer : 0.01 M MES (pH 6.0).

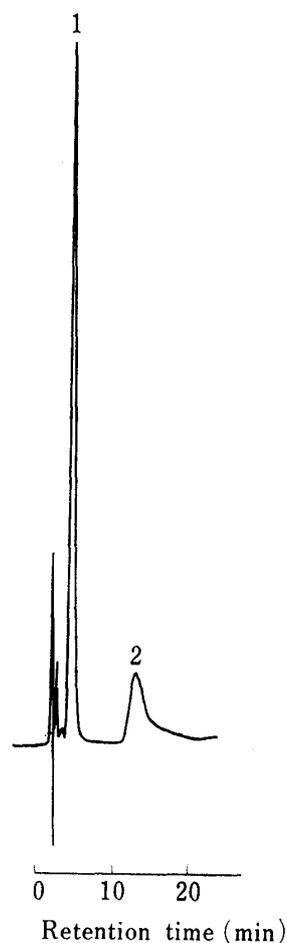


Fig. 2. Chromatogram of Malachite Green (MG) and MG-Sulfite Adduct by HPLC

1. MG-S adduct.  
 2. MG.

in ultra violet region. As shown in Fig. 1, the absorption at 317 nm attributed to the free MG decreased with an increase of the concentration of sulfite, while the absorption at around 254 nm attributed to MG-sulfite (MG-S) adduct increased.

The HPLC system used was composed of a KYOWA UV-spectromonitor KLC-220, a 3 mm (i.d.) $\times$ 300 mm pyrex glass column and a KYOWA MINI MICRO pump KSU-16H. The working conditions were; resin HITACHI #3010, eluent methanol/0.01 M 2-(N-morpholino)-ethanesulfonic acid (MES) (pH 6.0)/*n*-hexane (400/100/6, by volume), flow rate 0.7 ml/min, column pressure 20—23 kg/cm<sup>2</sup>, monitoring wavelength 254 nm. A typical chromatogram of MG-S adduct is shown in Fig. 2.

The pH of the solutions containing  $2 \times 10^{-4}$  M Na<sub>2</sub>SO<sub>3</sub> and  $5 \times 10^{-4}$  M MG were adjusted to 1.5, 3.6, 3.9, 4.2, 4.9, 5.5 or 6.0, with 0.01 N HCl or 0.01 N NaOH and the concentration of the adduct in each solution was determined by HPLC. The formation of the adduct was completed within one h at pH above 3.9, and the adduct remained stable at pH 3.6, 3.9 or 4.2 for 24 h.

A 0.1 M sulfite stock solution was prepared by dissolving a definite amount of Na<sub>2</sub>SO<sub>3</sub> in water just before use and standardized by iodometry. The standard sulfite solution was obtained by diluting the stock solution properly. Determination of sulfite concentration in the sample solutions was carried out by HPLC. The working curve for sulfite by peak height method was linear from  $2.0 \times 10^{-12}$  mol to  $1.2 \times 10^{-9}$  mol with a standard error below 5% in the proposed method.

Pyrosulfite (S<sub>2</sub>O<sub>5</sub><sup>2-</sup>) reacted with MG to form the same amount of adduct as that of sulfite, since pyrosulfite dissociated into sulfite in aqueous solution.<sup>6)</sup> Persulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) was also reactive, but the formation of adduct was slower than that of sulfite. Sulfate (SO<sub>4</sub><sup>2-</sup>), dithionate(S<sub>2</sub>O<sub>6</sub><sup>2-</sup>), pyrosulfate(S<sub>2</sub>O<sub>7</sub><sup>2-</sup>), sulfide(S<sup>2-</sup>) and thiocyanate(SCN<sup>-</sup>) gave adducts under the similar conditions.

The proposed method does not require the tedious procedures which are needed in colorimetric method such as West-Gaeke method, and would permit selective, sensitive and accurate determination of sulfite. Therefore, the proposed method may be applicable to estimate sulfite and its related compounds in environment such as air pollutants SO<sub>x</sub>, food additives and antioxidants for drugs. The authors are to analyse sulfite in drugs by the method. Further detail of the work will be given elsewhere in near future.

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