FPD-GC Determination of *S*-Methylmethioninesulfonium in Satsuma Mandarin Juice

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S-Methylmethioninesulfonium (MMS) is a precursor of dimethylsulfide (DMS) which is the characteristic component of the off-flavor produced from Satsuma mandarin juice. This paper describes a determination method for MMS based on flame photometric detector (FPD) and GC measurement of DMS produced by heat-treating Satsuma mandarin juice. Sodium borate buffer (pH 9.5) was added to an ampule containing Satsuma mandarin juice, then the ampule was sealed by flame and heated in an autoclave at 120℃ for 15 min to decompose MMS in the juice into DMS. The ampule was then put into a headspace vial containing ethylmethylsulfide as an internal standard. The headspace vial was immediately sealed with a plastic screw cap. The ampule was then broken in the vial. The headspace gas was analyzed by GC. This method has high accuracy and a good recovery.

Key words: *S*-methylmethioninesulfonium, Satsuma mandarin, dimethylsulfide, flame photometric detector, capillary gas chromatography.

S-Methylmethioninesulfonium (MMS) is widely distributed in nature and has been reported as a constituent of Satsuma mandarin, tomato, sweet corn, green tea, milk, soybean, asparagus and cabbage. MMS has prompted considerable biological and medicinal interest, and is a precursor of dimethylsulfide (DMS), which is the characteristic component of the off-flavor produced by heating Satsuma mandarin juice.[1,2] A determination method for MMS in Satsuma mandarin juice has previously been reported, the juice being directly supplied to a GC injection port heated at 200℃ DMS produced from MMS by heat degradation in the injection port was quantitatively analyzed by using a flame photometric detector (FPD), which is highly sensitive to sulfurcontaining compounds. The MMS content was calculated from the amount of DMS produced from MMS by heat degradation.[3]

This paper describes a determination method for MMS based on FPD-GC measurement of DMS produced by heat-treating Satsuma mandarin juice in an ampule.

The juice reamed from Satsuma mandarin was passed through a 20-mesh sieve. DMS dissolved in the juice was removed by bubbling nitrogen gas at a flow rate of 50 ml/min for 10min. Five ml of 0.1 M sodium borate (pH 9.5, Wako Pure Chemical Industries Ltd., Osaka, Japan) was added to a

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10-ml ampule containing 5-ml of the juice. The ampule was sealed by flame and heated in an autoclave at 120℃ for 15 min to decompose MMS in the juice into DMS. The ampule was then put into a 125-ml headspace vial containing 20 μl of ethylmethylsulfide (EMS, Fluka Chemie AG, Buchs, Switzerland) as an internal standard (0.5 mg/ml in 50% aqueous ethanol). The headspace vial was immediately sealed with a plastic screw cap, using PTFE (polytetrafluoroethylene) sheet on silicone rubber packing. Care needed to be taken with the packing material. If silicone rubber packing without PTFE sheet was used, the DMS and EMS vapor was adsorbed to the surface of the packing. The ampule was then broken in the vial by shaking and the vial was subjected for 15 min at 25℃ to shaking at 80 strokes/min. One ml of the headspace gas in the vial was introduced to an injection port with a 5-ml gas-tight syringe.

Standard samples of MMS were prepared. Ten ml of 0.1 M sodium borate buffer (pH 9.5) was added to each 10-ml ampule containing 5, 10, 20, 30, 40 or 50 μl of the 50 mg/100 ml aqueous solution of MMS-chloride (Tokyo Kasei Kogyo Co., Ltd., greater than 99% pure). The procedures following ampule sealing by flame are same as those described for the analytical sample preparations of Satsuma mandarin juice.

Analytical GC was performed on a Shimadzu GC-9A (Shimadzu Corp., Kyoto, Japan) instrument equipped with a flame photometric detector. The carrier gas was helium at a flow velocity of 24.5 cm/sec. The column temperature was isothermally maintained at 30℃ by using a CRG-9A low-temperature column controller (Shimadzu). The injection port and detector temperatures were 120℃, and the split ratio was about 9:1. The capillary column used was a 25m × 0.25mm (i.d.) fused silica HiCap-CBP 10 (Shimadzu), which is equivalent to a bonded OV-1701.

A typical chromatogram for Satsuma mandarin juice measured by FPD-GC is shown in **Fig. 1**. The retention times for DMS and EMS (internal standard) are in agreement with those of the standards. The relationship between the peak area ratio (Y) and concentration of sulfur compounds (X) is $Y^{(1/n)}=CX$, where n is an exponent and C is a constant.[4] The n value used in this study was 1.7,[5] and the regression equation obtained by the least squares method was $Y^{(1/1.7)}=0.03636\,X+0.00485$. Y and X are the peak area ratio (DMS/EMS) and MMS concentration (μM), respectively, the linearity being good

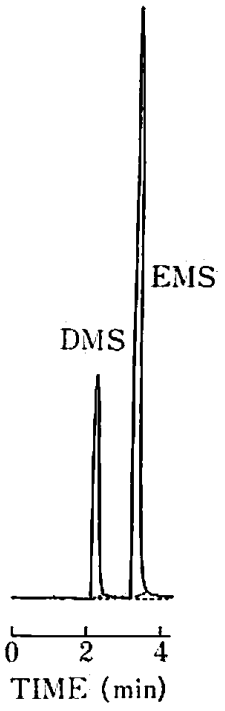

Fig.1. Typical chromatogram for Satsuma mandarin juice measured by FPD-GC.

(γ=0.9993). The coefficient of variation and the recovery of MMS from Satsuma mandarin juice were 0.79% and 100.2% for four measurements, respectively. The average value of MMS in Satsuma mandarin juice obtained by this method was 20.5 μM, this value agreeing with the value of 21.0 μM which has already been reported.[3)]

The results demonstrate that this method has high accuracy and a good recovery. In addition, the method is very useful for determining MMS in the homogenates of various foods and other materials containing insoluble matter.

References

1) M. Sawamura, M. Shimoda, T. Yonezawa and Y. Osajima: *Nippon Nōgeikagaku Kaishi*, 51, 7−13 (1977).
2) M. Sawamura, M. Shimoda and Y. Osajima: *Nippon Nōgeikagaku Kaishi*, 52, 281−287 (1978).
3) M. Shimoda, S. Ayano, H. Maeda, K. Suetsuna and Y. Osajima: *Nippon Nōgeikagaku Kaishi*, 58, 1217−1223 (1984).
4) C. H. Burnett, D. F. Adams and S. O. Farwell: *J. Chromatogr. Sci.*, 15, 230−232 (1977).
5) K. Tatsuka, S. Suekane, Y. Sakai and H. Sumitani: *Nippon Nōgeikagaku Kaishi*, 65, 875−877 (1991).