

Comparison of Solvent Extraction and Microwave Extraction for Release of Dimethyl Sulfide from Cereals and Canola

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Natural levels of dimethyl sulfide (DMS) in newly harvested wheat, barley, paddy, and canola were determined by gas chromatography using a flame photometric detector in sulfur mode. The two methods involved determination of DMS in the headspace of cereal or oilseed samples (1) after extraction with microwaves and (2) after a traditional approach using 25% KBr solution. Quantitative results from each method were similar, and therefore both methods are suitable for the determination of DMS in grains and oilseeds. However, the microwave procedure has several advantages; for example, results are obtained very quickly, and only a small amount of sample is required.

Keywords: *Dimethyl sulfide; microwave; extraction; analysis; cereal; canola*

INTRODUCTION

Dimethyl sulfide (DMS) is the most abundant of volatile sulfur species and widespread in its distribution (1, 2). It plays important roles in the global chemistry of the atmosphere and in the biogeochemical sulfur cycle (3). DMS naturally occurs in many foodstuffs and vegetables and contributes to the odor and flavor of many foodstuffs, including tea, cocoa, milk, wines, rum, beer, sweet corn, and numerous cooked vegetables (4–9).

DMS is analyzed by headspace analysis (6, 10) for solid commodities and by cold trapping (11, 12) for air or liquid samples. The method of boiling the solid sample in water and purging the DMS from solution into its gaseous state is also used. However, losses from enzymatic activity are inevitable (10). Potassium bromide (KBr) solution is suitable for extraction of DMS because enzymatic activity can be inhibited and DMS partitions into the headspace over KBr solution at a higher rate than over organic solutions (5, 13). Typically, it takes 10–20 h to completely extract whole grain with 25% KBr (13). This lengthy period can be a disadvantage in some situations. We therefore evaluated whether the procedure of DMS release by microwave extraction (MAE) of whole grain gives results more quickly than extraction of whole grain, as has been found previously for fumigant analysis (14).

MATERIALS AND METHODS

Samples. Four representative grains (wheat, paddy, barley, and canola) were used. The wheat was Australian Standard White (ASW, 11.2% moisture content, w/w, wet basis); Australian paddy was Waxy (10.7% moisture content); Australian barley was var. Schooner (11.5% moisture content); and Australian canola was Temora NSW (5.5% moisture content). All commodities were newly harvested (1999/2000) and insecticide-free.

Reagents and Apparatus. DMS and KBr (Ajax, Sydney, Australia) were purchased. Erlenmeyer flasks (250 mL) equipped with a ground-glass joint and a septum sampling system (Bibby Sterilin, Staffordshire, U.K.; catalog no. FE 250/

3) were used for extraction of sample and for preparation of fortified standard. Glass bottles (250 mL) equipped with Mininert valves (Alltech Associates, Deerfield, IL; catalog no. 9535) were used for MAE.

The microwave oven used for releasing DMS from commodities was a domestic model (Panasonic, Matsushita Electrical Industrial Co. Ltd., Osaka, Japan, model NN-5454) purchased at a local retail outlet. The maximum power output was 900 W at an operating frequency of 2450 MHz.

Determination of DMS was by a Shimadzu GC6AM GC (Shimadzu Seisakusho, Kyoto, Japan), equipped with a flame photometric detector (FPD). Separation was achieved on a 1 m × 3 mm i.d. glass column packed with HayeSep Q (Alltech Associates, Baulkham Hills, Australia; catalog no. 2801) at 110 °C and with a carrier flow (N₂) of 40 mL/min at 5.5 kPa.

Microwave Extraction Procedure. For evaluation of partitioning of DMS between sample and air and stability of DMS under MAE, DMS (2 μL of liquid) was injected into a 250 mL bottle containing 15 g of paddy. This resulted in a headspace concentration of 11.44 mg/L. The procedure of MAE as described by Ren and Desmarchelier (14) was carried out. The bottle was placed in the microwave oven and treated by MAE with output of 495 W for 30 s. After extraction, gas sample (60 μL) from the headspace was injected into the GC for determination of DMS concentration, and the bottle was left for 5 min before further extraction. The process of extraction and analysis was repeated four times.

The procedure of MAE for analysis of natural levels of DMS in the grains was the same as above, but the process of extraction and analysis was repeated until the amount of DMS in the headspace either remained constant or started to decline.

Levels of DMS were calculated on the basis of peak areas. The peak areas were calibrated periodically using a gas standard, and the data recorded in the figures are the mean of duplicate samples.

Solvent Extraction Procedure. Grain samples (50 g) were extracted in sealed flasks (250 mL) containing 50 mL of 25% KBr for 20–25 h. An aliquot of the headspace over the extraction solution (50 μL) was injected directly into the GC at timed intervals. The levels of DMS were calculated on the basis of peak areas. The peak areas were calibrated periodically using a spiked standard, and the data recorded in the figures are the mean of duplicate samples. Analysis of DMS in the headspace over solvent required complete elution of solvent vapor before further injections, so a minimum interval of 10 min was kept between injections.

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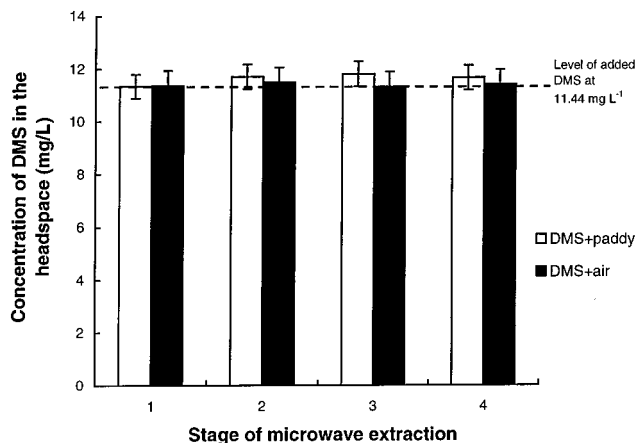


Figure 1. Partitioning of DMS between air and paddy sample and stability of DMS in both air and air plus paddy under microwave extraction (error bars indicate the standard error, $n = 2$).

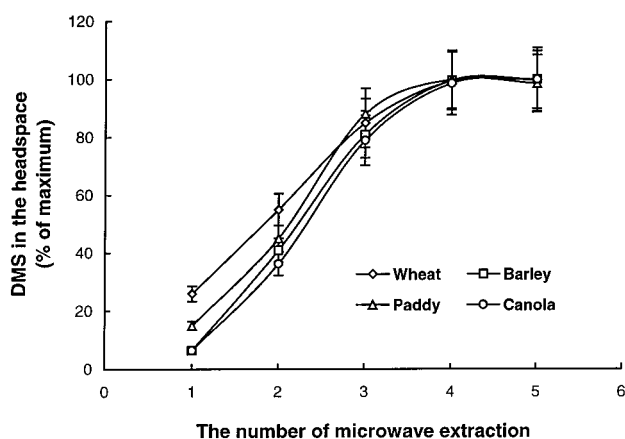


Figure 2. DMS released into the headspace by microwave extraction, calculated as percent of maximum residue in wheat, barley, paddy, and canola (error bars indicate the standard error, $n = 2$).

Preparation of Gas Standard and Fortified Samples.

The dilute gas was prepared by injecting a measured volume of liquid DMS into a bottle (250 mL) containing five glass beads (2–3 mm o.d.). After mixing, the diluted gas was used to prepare both fortified samples and gas standards. For extraction, spiked samples were prepared by injecting measured volumes of the diluted gas into a sealed flask containing commodity plus solution. Each spiked sample was duplicated.

RESULTS

Partitioning of DMS between Sample and Air and Stability of DMS under MAE. The concentrations of DMS in both air and the headspace over paddy after each microwave extraction are shown in Figure 1. In each case, gaseous concentrations of DMS remained constant. However, the concentrations of DMS in the headspace over paddy slightly increased after the initial MAE. This higher level of DMS could be due to release of naturally occurring DMS from the paddy sample.

Times and Power Setting of MAE for Release of DMS from Grains. Release of DMS from commodities after each extraction stage is shown in Figure 2. Maximum release of DMS was obtained by extraction for 120 s at 495 W. The patterns of release were similar for each commodity. The limits of detection of the microwave method are lower than those of the extrac-

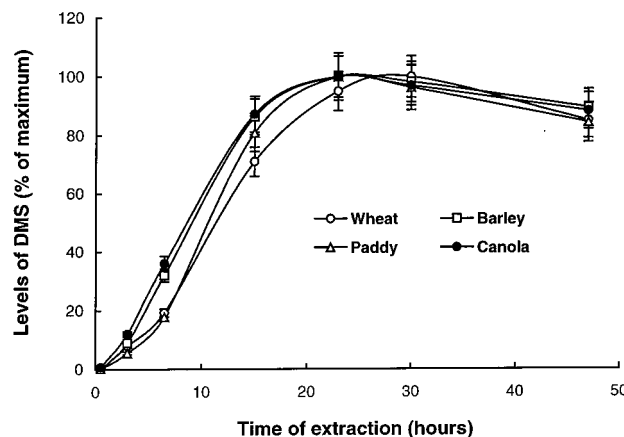


Figure 3. Extraction of natural levels of DMS in wheat, barley, paddy, and canola samples, plotted as the percentage of maximum levels of DMS versus time of extraction (error bars indicate the standard error, $n = 2$).

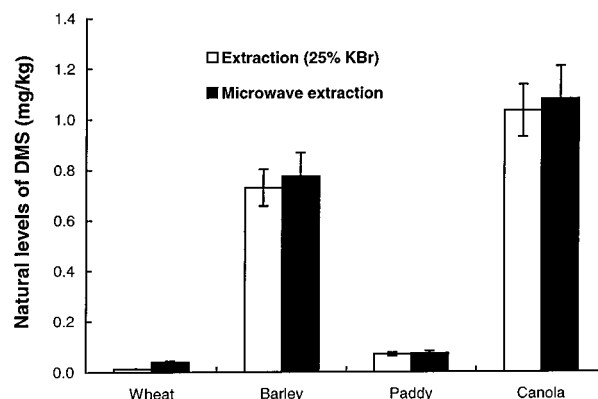


Figure 4. Natural occurrence of DMS in wheat, barley, paddy, and canola (error bars indicate the standard error, $n = 2$).

tion procedure, because the microwave releases almost all of the DMS from the matrix into the headspace. In contrast, only part of the DMS is present in the headspace after solvent extraction and the remaining DMS distributes into the solvent and the matrix. The higher sensitivity of the microwave method is important for the determination of natural levels of DMS.

Solvent Extraction Procedure. The concentration of DMS in the headspace over the 25% KBr solution plus wheat, barley, paddy, and canola is shown in Figure 3. Equilibrium partitioning between air was obtained after 20 h. The amount of DMS in the headspace increased over a period of 20 h and then declined slightly. The time of extraction for DMS to attain an equilibrium distribution between solvent and air was ~20–25 h.

Determination of DMS was corrected for recoveries of fortified sample using 25% KBr solution, and this fortified sample was used as a quantitative standard to calculate levels of DMS in grain samples. Desmarchelier and Ren (15) have discussed the use of fortified samples as standards.

Natural Levels of DMS in Commodities. DMS was found to be naturally present in wheat, barley, paddy, and canola (Figure 4). Results from each method (microwave extraction and solvent extraction) were similar. The levels of DMS in commodities varied with commodities. The values ranged from 0.04 to 0.10 mg/kg (ppm, w/w) in newly harvested (1999/2000) wheat and paddy and from 0.80 to 1.20 mg/kg (ppm, w/w) in newly harvested (1999/2000) barley and canola.

DISCUSSION

The results of the microwave procedure on paddy (Figure 1) indicated that almost all of the added DMS was released or partitioned into the headspace over the paddy sample and also indicated that DMS was stable under MAE in air or air plus paddy. That is, recovery at the power setting was ~100%. These results were confirmed with the other grain types (Figure 2). Because the microwave method releases almost all of the DMS from the matrix into the headspace, it is particularly suitable for the determination of natural levels of DMS in commodities (Figure 4). In summary, the microwave procedure satisfies the requirements for extraction of DMS. For example, recovery of fortified sample was adequate and DMS was stable under microwave extraction.

Use of microwaves to release DMS into the headspace involves the safety issue of increased temperature and pressure leading to (1) burning of the sample and (2) rupture of the container (although no such rupture has occurred in our laboratory). The optimal power setting needs to be determined on individual ovens, as they may vary with equipment. The microwave procedure has several advantages; for example, results are obtained very quickly, and only a small amount of sample is required, without the need to grind grain. However, from the point of view of safety, the MAE procedure should be confined to dry samples. In addition, as with the microwave procedure, a larger volume of gas sample can be injected into the GC and without solvent interference. This is especially important for determination of natural levels of DMS.

The solvent extraction method also gave good results (Figures 3 and 4), with levels of DMS similar to those found with the microwave method; however, the extraction period necessary was much longer, about two working days versus minutes. The time (~20–25 h) for complete extraction of DMS is similar to that for fumigants, such as carbonyl sulfide (COS) and carbon disulfide (CS₂) (15). However, there are several advantages in using a solvent extraction method, such as possible multiresidue methods and application for both dry and wet samples.

Choice of method for determination of DMS depends on circumstances. Both methods enable determination of DMS and have special advantages.

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