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Evaluation of a Mixed-Phase Column Packing for the GC Determination of Fumigant Residues in Grains

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During our analyses for fumigant residues in stored grain crops from a domestic food survey, combinations of residues such as carbon tetrachloride and chloroform could not be satisfactorily separated on recommended gas chromatographic columns, e.g., 4.0 m 15% UCON LB 500X or 3.8 m 15% OV-17 (CLOWER 1980). Quantifying a small fumigant response which appeared as a shoulder on a larger one was difficult because of the masking effects of the larger residue.

In our search for column packings that could fully separate commonly detected residues, we found that a 20% OV-101 packing is satisfactory. To provide a second column on which fumigant residues could be confirmed, we tested a 20% OV-225:20% OV-17 (2:1) mixed-phase packing. A 1.8 m column packed with this mixture yielded an elution profile that is differentiated from those of 20% OV-101 or 20% OV-17 columns of the same length. Baseline separation was achieved for seven fumigants investigated: carbon tetrachloride (CCl_4); chloroform ($CHCl_3$); trichloroethylene (TCE); ethylene dichloride (EDC); tetrachloroethylene or perchloroethylene (PCE); chloropicrin (CP); and ethylene dibromide (EDB). Four working-solvent media: isooctane; acetone; hexane; and acetone:water (5+1), were tested for their elution placement with respect to grain fumigants, and each chromatographed before the analytes of interest on the mixed column. The (2:1) packing mixture is durable. Preparations are easily duplicated.

MATERIALS AND METHODS

Grain samples (20 lb) were collected annually from storage bins or railroad cars enroute to mills and placed under freezing conditions (-14°C) for analysis. Fumigant residues were extracted by leaching the whole-kernel grain samples according to the current AOAC method (AOAC XIII 1980), i.e., 50 g portions were soaked for two days in acetone:water (5+1) solution. Two mg sample equivalents were then screened in one of the following ways: a) by direct injection of the acetone:water leachate if the determinative step was performed immediately following the extraction of the grain sample, or b) by injection of an isooctane solvent which is used to partition fumigant residues from the leachate. The partitioning step was employed when there was to be any delay between the extraction and chromatography steps because fumigant residues are gradually lost in the acetone:water solution (DAFT 1983).

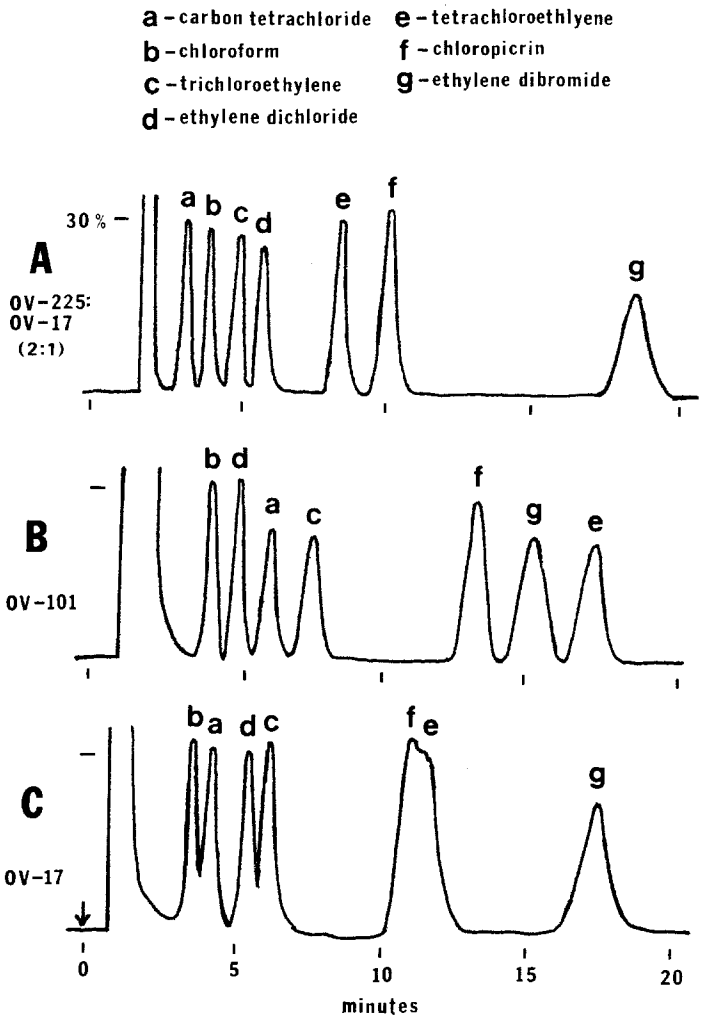

Figure 1. Elution orders from 1.8 m column packings of: A) (2:1) mixture of 20% OV-225:20% OV-17; B) 20% OV-101; and C) 20% OV-17. Fumigant peaks are: a, 0.38 ng CCl_4; b, 2.2 ng $CHCl_3$; c, 2.3 ng TCE; d, 151.0 ng EDC; e, 1.3 ng PCE; f, 3.5 ng CP; and g, 5.9 ng EDB. Solvent fronts from columns are: A) isooctane; B) acetone:water (5+1); and C) acetone.

The gas chromatograph (GC) used was a Tracor 560 equipped with dual constant current ^{63}Ni electron capture detectors and 1.8 m X 4 mm id glass columns. Operating conditions were: injector ports, 125-225°C; columns, 75-85°C; detectors, 350°C; carrier gas flows, 30-50 mL/min; chloroform retention times (t_R), 3-4 min; sensitivity, 30% full scale deflection for 2 ng chloroform; output attenuations, 50-100X at saturation current settings of 8.5 X 10^{-9} amps; recorders, 1 mV full scale, 12.7 mm/min chart speeds.

The column packings studied were: (A) a phase mixture of 20% OV-225: 20% OV-17 (2:1); (B) 20% OV-101; and (C) 20% OV-17, each on Chromasorb W(HP), 80-100 mesh, and conditioned at 240°C for 72 hours. Fumigant elution sequences for each packing are shown in Figure 1. If a similar sequence is not found for the (2:1) mixed packing, then it can be adjusted by adding small amounts of one of the corresponding phases to the mixture. Adding the 20% OV-225 preparation changes the elution pattern by moving carbon tetrachloride towards the point of injection and away from the chloroform peak. Adding 20% OV-17 reverses this pattern. Adjustment is correct when these two peaks are cleanly separated as in Figure 1-A. Phase increments of about 1/2 g per seven grams of mixture are added should adjustment be necessary.

RESULTS AND DISCUSSION

Grain fumigants generally are volatile, low-boiling compounds. A problem that occurs in the GC portion of this analysis is finding a working solvent in which fumigant residues are stable and one, which at the same time, does not co-elute with the analytes in question. Working solutions of acetone, for example, in which residues are lost, happen to elute before grain fumigants on the three columns of this study. Conversely, residues in a working solvent of isooctane remain unchanged up to 30 days, but isooctane tends to elute in analyte regions on the single-phase columns. Sometimes the elution rates of isooctane from these columns can be controlled by precise regulation of injector port temperatures, but the resultant rate changes are usually small and the technique is not dependable for the separation of working solvents and incurred fumigant residues.

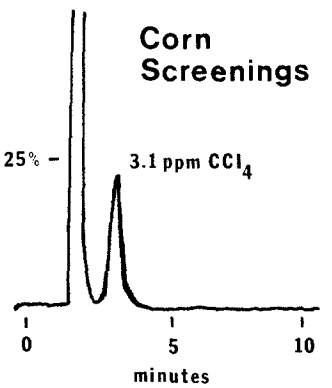

Figure 2. Chromatogram of corn screenings (kernel/cob fragments & dust), 0.1 mg; working solvent: isooctane.

On the (2:1) mixed column however, isooctane chromatographs as a typical front, i.e., as the first major response following injection and in front of analyte retention regions. So an advantage in conduct-

ing fumigant determinations with the mixed column is the ability to utilize a sample matrix which is well suited to both analyte stability and analysis by gas chromatography.

The (2:1) packing mixture is durable. For the past three years, we have employed one mixed column without noticeable changes in peak shapes or retention patterns. If the column is dismantled or stored between assays, we condition it in the chromatograph at 200°C before using.

In checking the column for reproducibility at the 80°C operating temperature for fumigant analysis, we made triplicate injections of standard solutions of the seven grain fumigants. Injections were made in two-hour periods on different days. Replicate injections of grain sample extractions which contained one or more incurred residues were also made. The overall variation for fumigant retentions and peak heights is less than 5%.

The main advantage of this column however, is its capacity for transposing the elution order of fumigants from those of the 20% OV-101 and 20% OV-17 columns, Figures 1-B & C. When these other columns are used with the mixed column during analysis, incurred fumigant residues are confirmed with a greater degree of certainty.

Grain sample chromatograms from the mixed column are shown in Figures 2 & 3. Residues of carbon tetrachloride (Figure 2) are detected frequently at levels between 1-10 ppm. Combinations of chloropicrin and ethylene dibromide (Figure 3) are sometimes added to stored

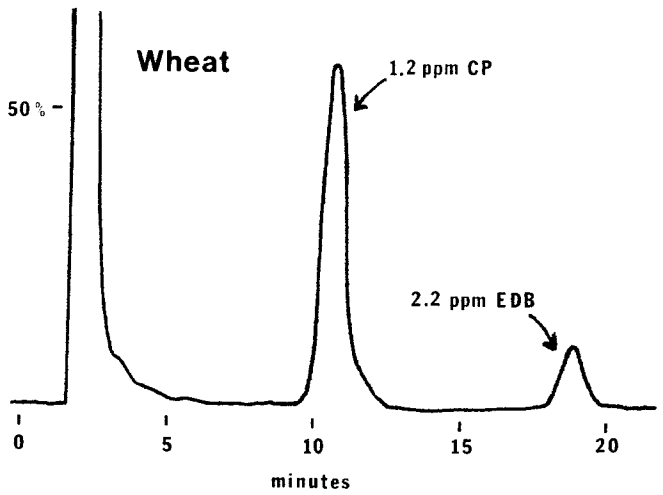

Figure 3. Chromatogram of a wheat sample, 2 mg; working solvent: acetone:water (5+1).

grains. As many as four residues can appear on a chromatogram, usually because the grain had been fumigated more than once with different compounds.

Conclusion

A 1.8 m mixed-phase column of 20% OV-225:20% OV-17 (2:1) separates the residues of seven grain fumigants and interchanges their elution order from that of 20% OV-101 or 20% OV-17 single-phase columns. A working solvent of isooctane in which fumigant residues are stable, chromatographs in front of the analytes on the mixed column. These combined characteristics make the mixed column suitable for the determination of fumigant residues of stored grains.

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