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Removal of GC Background Interferences from Reagents Used in Fumigant Analysis

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A problem with current gas chromatographic methods for determining fumigants in grain and grain products (Heuser & Scudamore 1968; AOAC 1980; Malone 1969, 1970; Clower 1980; Rains & Holder 1981; Hughes et al. 1983; Heikes 1984) is background interferences caused by the reagents used in these methods. For example, 1-1000 ppb (ng/g) of chloroform, carbon tetrachloride, ethylene dichloride, or tetrachloroethylene are frequently detected in the pesticide-grade acetone used for leaching fumigant residues from grain by the AOAC method. If a 2,2,4-trimethylpentane partition is employed to remove analytes from this leachate (Daft 1983) or a hexane partition to remove 1,2-dibromoethane (EDB) from a blended-type sample extraction (Newsome & Panopio 1977) then 10-ppb levels of these background interferences are sometimes detected in the partitioning solvents. These interferences are also detected in the reagents used with recently improved co-distillation procedures (Ferm & Proehl 1984; Larson et al. 1984; Ruhland & Hughes 1984). Furthermore, these background contaminants and additional residues of 1,1,1-trichloroethane or trichloroethylene can be intermittently detected in the deionized water which is used in all of the methods cited above.

Quality control of multiple-residue fumigant determination at 1-1000 ppb levels depends on using interference-free reagents. This report describes procedures for removing background contaminants from these reagents. Nitrogen gas is used to purge volatile contaminants from deionized water, 10% phosphoric acid in water, and 30% glycerin in water. Alumina chromatography (Underwood J, USFDA, Kansas City, MO; Iwata et al. 1983) is used to remove interferences from 2,2,4-trimethylpentane. Liquid-liquid partitioning followed by azeotropic redistillation is used to purify acetone.

MATERIALS AND METHODS

The reagents used were 1) deionized water, 2) 10% phosphoric acid (v/v), 3) 30% glycerin (v/v), 4) pesticide-grade 2,2,4-trimethylpentane, 5) fresh Alumina-I (basic and neutral), 6) pesticide-grade acetone, 7) sodium chloride, and 8) anhydrous sodium sulfate. A rheostat-controlled 5-L distillation apparatus with a 45-cm reflux column packed with glass beads (Sics U, USFDA, Kansas City, MO) was used to distill the partitioned acetone solution.

The gas chromatograph used was a Tracor 560 equipped with a Ni-63 electron capture detector and a 1.8 m X 4 mm id glass column packed with 20% OV-225:20% OV-17 (2+1 mixed bed) or 20% OV-101 (single bed), each on 80-100 mesh Chromosorb W(HP). GC conditions were: injector port 150-220C; column 75-90C; detector 350C; and carrier gas flow (5% methane in argon) 50-65 mL/min. Recorder attenuation was 10X; chart speed was 10-12.7 mm/min. Sensitivity was about 30% full scale deflection for 0.05 ng chloroform.

The fumigant method used was a modified procedure of the AOAC (Daft 1983). Grains were leached with 5+1 acetone:water while grain products were leached with a 1+4 acetone:water solution which also contained 5% phosphoric acid, 10% sodium chloride (w/v), and 1% glycerin. An aliquot of either leachate was then partitioned with trimethylpentane at a 1:1 to 5:1 ratio, drying this final sample matrix over anhydrous sodium sulfate. (Note: A slightly acidified leaching solution enhances the stability of fortified methyl bromide and chloropicrin residues. Sodium chloride and glycerin are also stabilizing agents and are aids for extracting:partitioning residues from nonfatty foods.)

Reagent cleanup procedures were as follows: 1. Deionized water was purged with nitrogen (or filtered air) at 90C for 2-3 h. 2. The 10% phosphoric acid and 30% glycerin each was purged with nitrogen at 80-90C for 4-5 h. Water lost though evaporation was replaced with interference-free water. 3. Five liters of trimethylpentane were passed through two successive columns of activated Alumina-I. The top column contained 100 g of Alumina-I (basic); the lower one contained 100 g of Alumina-I (neutral). 4. Acetone was partitioned with trimethylpentane as follows: 700 mL of acetone were added to a 4-L blender with 2400 mL deionized water (unpurged), 200 g NaCl, and 150 mL relatively clean trimethylpentane. The mixture was blended 1 min at medium speed and transferred to two 2-L separatory funnels. The lower aqueous portion was re-partitioned (re-blended) three more times with 150-mL portions of

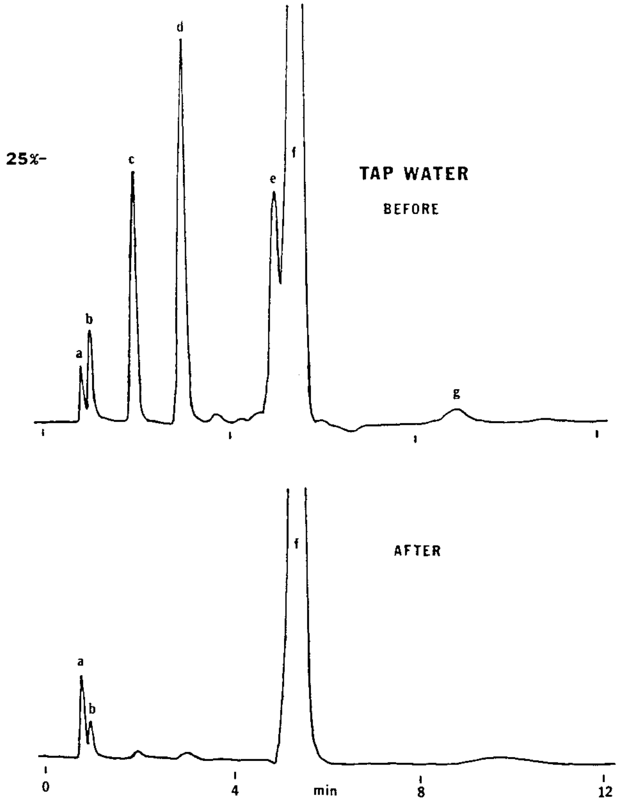

Figure 1. Chromatograms of tap water before and after nitrogen purging of volatile background contaminants: a) air, b) unknown, c) 28 ppb dichloromethane, d) 3 ppb chloroform, e) unknown, f) trimethylpentane peak, and g) unknown; 20% OV-101, 75C.

trimethylpentane, discarding the trimethylpentane each time. The aqueous acetone portion was then distilled, discarding the first 100 mL of distillate and shutting down the apparatus when the vapor temperature rose above 56C. The azeotrope comprised about 98% acetone: 2% water. (Note: The trimethylpentane used in this step could not be recycled through alumina because it contained small amounts of acetone.)

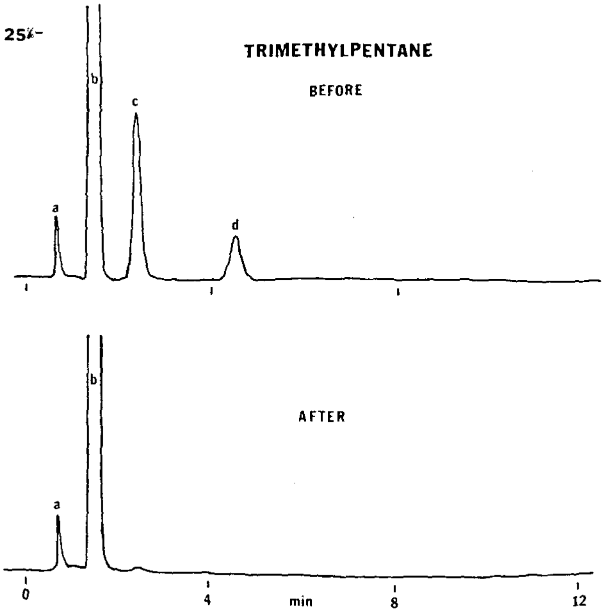

Figure 2. Trimethylpentane before and after alumina chromatography: a) air, b) trimethylpentane peak, c) 5 ppb chloroform, and d) 1 ppb tetrachloroethylene; 20% OV-225:20% OV-17 (2+1), 90C.

RESULTS AND DISCUSSION

Chloroform was the most difficult contaminant to remove from all reagents, especially acetone. For example, when 1-ppm chloroform was present in the originally purchased acetone, a 1-ppb level usually persisted after cleanup. Chloroform was more easily removed from the other reagents, but the best way to eliminate this contaminant from reagent blanks is to find reagents that contained none in the first place.

Our laboratory water which is deionized with ion-exchange resins usually contained much fewer background interferences than our tap water, but in either case

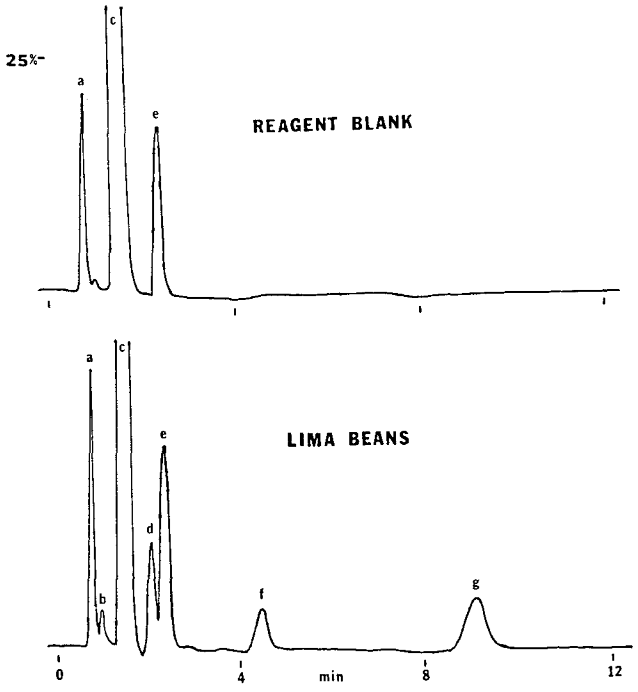

Figure 3. Chromatograms of reagent blank and lima bean sample (7 mg) following reagent cleanup: a) air, b) unknown, c) trimethylpentane solvent peak, d) 1 ppb carbon tetrachloride, e) approx. 6 ppb chloroform background peak, f) 1 ppb tetrachloroethylene, and g) 9 ppb dibromoethane (EDB); 20% OV-225:20% OV-17 (2+1), 90C.

the inert-gas purging of volatile contaminants was effective as shown in Figure 1. Other published methods for removing organic contaminants from large amounts of water utilize macro-reticular resins (Fritz 1983; Albright R, Rohm and Hass, Philadelphia, PA). We have not tested these methods.

The removal of interferences from trimethylpentane worked best when the alumina was fresh (see Figure 2).

Our earlier attempts to do so using alumina that was several years old did not remove these background contaminants from trimethylpentane. For test purposes, about 500 mL of hexane were also purified using fresh Alumnia-I although hexane is not used in the fumigant method of this study.

Gas purging did not effectively remove volatile contaminants from acetone:water solutions. Since acetone solution works well for leaching whole-kernel grain samples, the partition:redistillation cleanup procedure was used to ensure sufficient quantities of pure acetone for this analyis.

A reagent blank resulting from the cleanup procedures of this report is shown in Figure 3. Interferences of dichloromethane, carbon tetrachloride, and tetrachloroethylene have been successfully removed from all reagents. Yet, a chloroform interference peak is shown to persist. About 40% of this peak came from contaminated phosphoric acid which was later gas purged as 10% solution. The remainder of this interference came from the original acetone.

In conclusion, the GC background interferences caused by reagent contamination has brought about a trend towards using minimal reagent, e.g., headspace (Entz & Hollingfield 1982; Page & Charbonneau 1984), sweep- and acid reflux distillations (Malone 1969;1970), purge-closed loop (Wang & Lenahan 1984), steam or co-distillation (Rains & Holder 1981; Ferm & Proehl 1984; Larson et al. 1984; Ruhland & Hughes 1984), and sparge and trap (Heikes 1984). But presently, the simultaneous determination of 10 or more fumigants in whole-kernel grain still requires reagent media which effectively extract these residues while providing analyte stability. Analysts need dependable supplies of pure reagents.

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