Determining Propoxur and Other Carbamates in Meat Using HPLC Fluorescence and Gas Chromatography/Ion Trap Mass Spectrometry after Supercritical Fluid Extraction

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Supercritical fluid extraction (SFE) using CO_2 was examined for separating carbamate pesticides from interfering coextractives prior to analysis either by liquid chromatography with fluorescence detection or by gas chromatography/ion trap mass spectrometry (GC/ITMS). Pre-extraction of the ground meat with acetonitrile prior to SFE left behind over 99% of the fat and fiber in ground meat. The concentrated acetonitrile extracts containing the carbamates and other coextractives were adsorbed on a pelletized diatomaceous earth for SFE. SFE further reduced the amount of coextractives 10-fold. This procedure allows larger, more representative samples to be routinely analyzed, removes interferences that appear in the fluorescence mode, and reduces many of the non-volatiles that can accumulate on the capillary column in the GC/ITMS mode and shorten its lifetime after multiple injections.

Keywords: *Food safety; vapor pressure; sorption; insecticides; residues; fluorescence SFE; ITMS; meat; GC*

INTRODUCTION

Short-term environmental persistence and the lack of accumulation within organisms led to the use of *N*-methylcarbamate insecticides as alternatives to the organochlorine insecticides used in the 1940s and 1950s to which insects were developing resistance. Because the established tolerance levels for carbamate insecticides in meat are low, and metabolism in animals is high, contamination of meat may occur only because of accidental or deliberate adulteration. Recently, a committee on pesticides in the diets of infants and children (National Research Council, 1993) recommended that all dietary as well as nondietary exposures to pesticides, including exposure to air, dirt, indoor surfaces, lawns, and pets, be considered when potential risks are assessed.

CO_2 has been used as a supercritical fluid for extracting fats and other fluid-soluble chemicals from various matrices.

Upon depressurization, the fluid returns to its gaseous phase, allowing the extracted solutes to be collected by trapping on a solid surface or in a solution. Animal tissue matrices contain various lipids at different concentrations depending on tissue type. The selective extraction of an analyte from lipids using supercritical CO_2 is extremely difficult (Murugaverl et al., 1993). Maxwell et al. (1993) determined nitrosamines in frankfurters after supercritical extraction (SFE). Snyder et al. (1993) used SFE for poultry tissue. Chlorinated pesticides were subsequently determined in the fat-containing extracts after cleanup using liquid chromatography.

The purpose of this study was to develop methodology using SFE for determining after minimal cleanup residues of carbamate insecticides above tolerance levels in meat or meat products for regulatory use. The application of SFE to residues in animal tissues has been limited by the small sample sizes that can be used and by coextraction of fat which must be removed prior to analysis. The present procedure, by using a preliminary acetonitrile extraction, overcomes both of these problems.

Propoxur, a carbamate insecticide, was selected as a model compound for this study since it is an inhibitor of cholinesterase (Mineau, 1991) and is registered for use by certified applicators for the control of indoor pests.

MATERIALS AND METHODS

Standards. Propoxur 97%, carbaryl 99.6%, aldicarb 99.7%, methomyl 98.9%, carbofuran 99.5%, and 3-hydroxycarbofuran 95% were obtained as reference standards from the Environmental Protection Agency. Analytical standard solutions of 1 mg/mL were prepared in HPLC grade acetonitrile and stored in the refrigerator. Fortification solutions were made from dilutions of the standards. Chrysene-d_{12} (Cambridge Isotope Laboratories, Woburn, MA) was used as an internal standard. Propoxur, 2 μg/mL, and chrysene-d_{12}, 100 μg/mL, in acetonitrile were used for fortifying samples and preparing three calibration standards, each containing 100 ng/mL of chrysene and either 50, 100, or 200 ng/mL of propoxur. Fifteen microliters of the internal standard chrysene-d_{12} was added to the glass vials that contained the 1.5-mL acetonitrile eluate from the SFE trap prior to injection for analysis by gas chromatography/ion trap mass spectrometry (GC/ITMS).

Materials. Ground beef was obtained through the Meat Science and Dairy Science Laboratories (USDA, ARS, Beltsville, MD) from animals that were not exposed to carbamate insecticides. SFC/SFE grade CO_2 (Air Products, Allentown, PA) was used for SFE. A lower grade of CO_2 was used for cryogenic cooling of the SFE trap and for the septum-programmable injector on the GC/ITMS. Chem Elut-Hydromatrix (Celite 566, a pelletized diatomaceous earth) was obtained from Varian Sample Preparation Products Co., Harbor City, CA. Dispersing the sample with Hydromatrix enhances SFE of both analytes and lipids (Hopper and King, 1991).

Oleic acid was obtained from J. T. Baker Chemical Co., Phillipsburg, NJ, tristearin, monostearin, and monoolein was obtained from TCI America, Inc., Portland, OR. and lecithin and bovine free and conjugated bile acids from Sigma, St. Louis, MO.

Pre-extraction of Ground Meat with Acetonitrile. Samples consisting of 100 g of ground beef were blended with 200 mL of acetonitrile for 1 min and filtered through 9-cm Whatman No.1 filter paper under gravity to remove the fat and fiber. The filtrate was transferred to a separatory funnel and extracted twice with 25 mL of hexane saturated with acetonitrile. Three milliliters of the hexane-washed extract was considered to be equivalent to 1 g of ground beef. Samples were fortified at 0.01, 0.05, and 0.1 ppm levels by adding microgram amounts of the propoxur standard in acetonitrile directly to the ground beef in the blender. Aliquots of 3-, 30-, and 90-mL were transferred to 125-mL Erlenmeyer flasks each containing 2 g of Hydromatrix. The solvents were evaporated under water aspiration. The Hydromatrix was transferred to extraction thimbles, and the SFE extraction proceeded as described. The 3-mL aliquots, representing 1 g of ground meat, was used for detecting propoxur using the GC/ion trap procedure.

Supercritical Fluid Extraction. A Model 7680T SFE module (Hewlett-Packard, Avondale, PA) was used that included an automated variable restrictor and a solid phase sorbent trap prepacked with 30 μm of Hypersil ODS into which the carbon dioxide extraction solvent was decompressed during collection. CO_2 density was 0.85 g/mL at an extraction pressure of 329 bar at 60 °C. The 7-mL extraction thimble was dynamically extracted with CO_2 at a flow rate of 1.6 mL/min following an initial 2-min static extraction for a total of five thimble volumes. The nozzle temperature was 50 °C, and the sample extract was collected on a 1-mL ODS sorbent trap at 9 °C. The extracted sample was eluted from the trap with 1.5 mL of acetonitrile at 0.4 mL/min and a trap temperature of 50 °C and collected in 2-mL glass vials placed in a fraction collector. The ODS trap was regenerated between extractions by rinsing with 2 mL of ethyl acetate followed by 2 mL of acetonitrile at 1 mL/min to waste. The time for the extraction/elution procedure per sample was approximately 30 min.

HPLC Fluorescence Detection. An Isco Model 2350 HPLC pump (Isco, Inc., Lincoln, NE) containing a 50-μL loop injector and a 5-μm particle size, 150 × 4.6 mm Shandon Hypersil Green Env C-8 bonded column (Alltech Associates, Inc., Deerfield, IL), was used. The mobile phase was operated isocratically with 40% acetonitrile and 60% water. The eluate was fed into a three-way tee within a Timberline RDR-2 postcolumn module (Timberline Instruments, Boulder, CO). The reagent, consisting of 25 mg of *o*-phthalaldehyde and 180 mg of Thiofluor (Pickering Laboratories, Inc., Mountain View, CA), *N*,*N*-dimethyl-2-mercaptopropionic acid, was mixed in 250 mL of 0.05 M sodium hydroxide and prepared fresh daily according to the directions of Simon et al. (1993). No degassing of the reagent was required since the module operated under helium pressure. The third plug of the tee was sealed with a dead-end nut since the single-stage postcolumn fluorescence HPLC method for the analysis of *N*-methylcarbamates as described by Simon et al. (1993) was chosen. The effluent from the module was directed into a HP1046A fluorescence detector (Hewlett-Packard, Wilmington, DE) operated at an excitation wavelength of 250 nm, an emission wavelength of 450 nm, a photomultiplier gain of 13, and a flash lamp of 1.5 W. The signal was fed into a Gateway 2000 486-33C computer (Gateway 2000, N. Sioux City, SD) containing an IscoChem Research interface card (Isco, Inc.).

Gas Chromatography–Mass Spectrometry. A Finnigan MAT Model ITS40 ion trap (Finnigan MAT, San Jose, CA) with a Varian 3300/3400 gas chromatograph equipped with a DB-5ms capillary column (J&W Scientific, Folsom, CA) (30 m, 0.32 mm i.d., 0.25 μm film thickness), a 5-m phenyl-methyl deactivated (Restek Corp., Bellefonte, PA) guard column (0.32 mm i.d.), and a CTC A200S autosampler (Finnigan MAT) was used. One-microliter aliquots of solutions of standards and samples in acetonitrile were injected into a Model 1093 (Varian, Walnut Creek, CA) septum programmable injector with a 3-s needle hold time in port before injection. The injection port was held at 55 °C for 30 s and then taken to 230 °C in 1 min. The helium column head pressure was 5 psi. The initial oven temperature was held at 55 °C for 30 s and then ramped to 125 °C at 50 °C/min and to 250 °C at 3 °C/min. It was then held at 250 °C for an additional 4 min. The transfer line was heated to 240 °C, and the detector manifold was heated to 215 °C. Autotune calibration was performed before each injection sequence: electron impact mode, 10-μA filament current, 1850-V electron multiplier tube, 1-ms ion time, automatic gain control at 20 000. Mass spectra were acquired at *m/z* 70–420 from 3 to 47 min after injection. A Magnum version 2.4 software package and a Gateway 2000 computer (Gateway 2000) were used for data acquisition, processing, and instrument control.

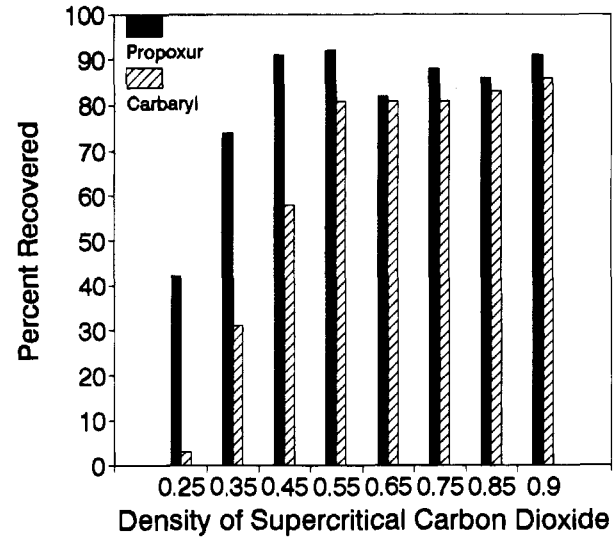

Figure 1. Recovery of propoxur and carbaryl standards after extraction with supercritical CO_2 at various densities followed by elution of the ODS trap with acetonitrile. Propoxur (1.74 mg) and carbaryl (1.0 mg) were adsorbed on 20 g of Hydromatrix; 2 g of impregnated matrix was extracted; 1 mL of water was added to Hydromatrix prior to extraction.

Lipid, Carbaryl, and Propoxur Analysis. Lipids extracted with acetonitrile and with CO_2 were analyzed gravimetrically after evaporation of the solvent. Carbaryl was analyzed by diluting 150-μL aliquots of the 1.5-mL acetonitrile rinse with 10 mL of 0.25 N sodium hydroxide and monitoring the fluorescence intensity (Argauer and Bontoyan, 1970). Propoxur was analyzed according to two methods, one using HPLC with a postcolumn hydrolysis to methylamine and formation of the fluorescent isoindole derivative (Moye et al., 1977; Krause, 1985; McGarvey, 1989; de Kok and Hiemstra, 1992; Page and French, 1992; Simon et al., 1993) and the other using ITMS (Cairns et al., 1993).

RESULTS AND DISCUSSION

Principle. Carbamate insecticides are moderately polar and soluble in acetonitrile. The preliminary extraction of ground meat samples with acetonitrile and partitioning with hexane remove and concentrate the carbamate insecticide residues present in the meat samples while leaving over 99% of fats and fiber behind. Pre-extraction permits larger sample sizes to be taken and thus assures more representative sampling while removing a substantial amount of fat that interferes in the SFE extraction. The size of aliquots from the acetonitrile pre-extraction is based on the optimal signal to noise ratio of the HPLC fluorescence and the GC/ion trap detectors and on the amount of coextractives present that may cause contamination of the GC/ion trap detector.

SFE Density of CO_2. The CO_2 density was varied between 0.3 and 0.9 g/mL to determine the effect of recovery for the carbamates. The data in Figure 1 show that extraction at a 0.3 g/mL CO_2 density produced low recoveries of carbaryl and propoxur standards. When pressure and temperature were adjusted to a CO_2

Table 1. Percent of Lipid and Matrix Recovered after Evaporation of Extraction Solvents As Determined by Gravimetric Analysis

lipid sample extracted	extraction solvent: 80% acetonitrile, 20% water,[a] then washed twice with hexane after extraction	SFE solvent: supercritical CO_2[b]
oleic acid	<1	
tristearin	<1	
monostearin	46	60 (trap clogged)
monoolein	51	56
lecithin	<1	<1
bovine free and conjugated bile acids	99+	<1
ground beef	<1	<0.1[c]

[a] One-gram lipid samples were extracted. [b] 50–400-mg lipid samples were extracted with superfluid CO_2, density 0.85 g/mL. [c] Residue from acetonitrile pre-extraction (300 mg) adsorbed on Hydromatrix. Total removed based on a 100-g meat sample.

density of 0.85 g/mL, maximum extraction was achieved. Unfortunately, increasing the density of CO_2 also increases the efficiency of extraction of lipids (Hierro and Santa-Maria, 1992). The level of extraction of lipids with supercritical CO_2 continually increases between densities of 0.40 and 0.60 g/mL (Gere and Derrico, 1994).

Matrix Coextractives. Table 1 shows the usefulness of pre-extracting meat samples with acetonitrile prior to SFE. Over 99% of the fatty acids, triglycerides, and phospholipids, represented by the model lipids oleic acid, tristearin, and lecithin, are left behind. Unfortunately, half or more of the monoglycerides present in the lipid sample are expected to be carried over to the Hydromatrix and are readily extracted by supercritical CO_2. The monoglycerides, after being extracted by CO_2, were trapped on an ODS solid support, permitting some further cleanup of this problem coextractive. Pre-extraction with acetonitrile and evaporation of the solvent decreased the bulk of a 100-g ground beef sample to 300–500 mg. SFE followed by elution of the ODS trap with 1.5 mL of acetonitrile further reduced the amount of coextractives to less than 50 mg.

Effect of SFE on HPLC Fluorescence Chromatograms. Figure 2 compares chromatograms obtained for ground beef fortified with propoxur at 0.1 mg/mL (0.1 ppm). An injection of the hexane-washed filtrate from the acetonitrile pre-extraction is compared with a 60 times more concentrated injection after SFE cleanup. Clearly SFE removed a major portion of interfering coextractives that eluted early in the run and formed fluorescent derivatives with the postcolumn reagent. Since the acetonitrile extract contains approximately 20% water, some amino acids may have been extracted from the ground beef. These were removed by SFE. Since 90 mL of the pre-extracted hexane-washed filtrate was adsorbed on 2 g of Hydromatrix prior to SFE, the peak area at the retention time for propoxur in chromatogram C can be quantitatively compared with the standards in chromatogram B. Since 3 mL of the hexane-washed acetonitrile is taken to be equivalent to 1 g of fortified meat, the recovery of propoxur is 95%.

Sorption of Propoxur Vapor by Ground Beef in an Enclosed Environment—a Worst Case Scenario. Ground beef may be left to defrost in a well-ventilated room prior to cooking. The room may contain propoxur vapor as a result of treatment for control of cockroaches and other insects. Experiments were performed to determine what amount of propoxur vapor, if any, may be sorbed by a ground beef patty under

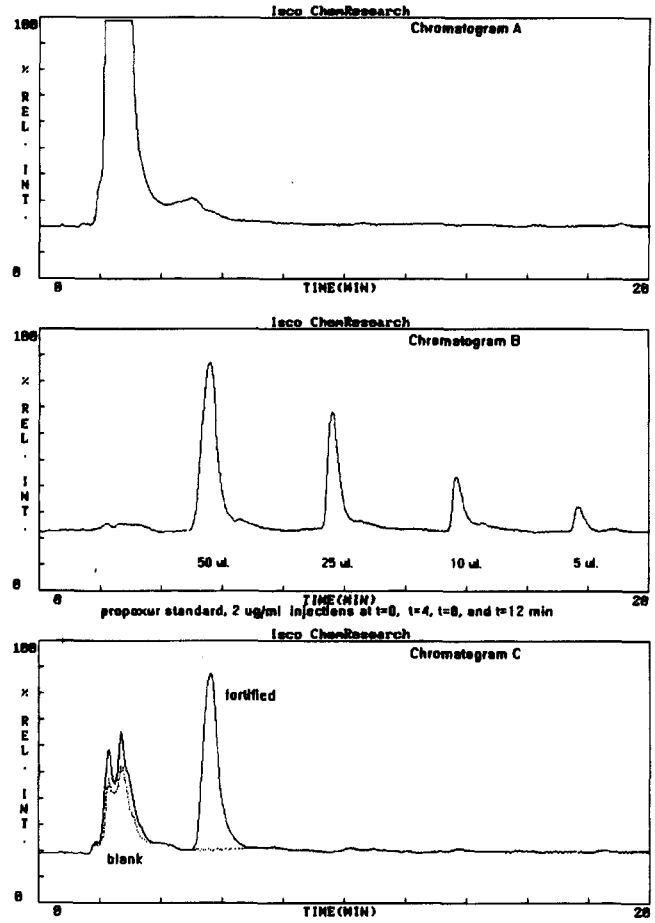

Figure 2. HPLC fluorescence chromatograms of propoxur recovered from ground beef fortified with propoxur at 0.1 mg/kg. Chromatogram A: 50-μL aliquot of the hexane-washed acetonitrile filtrate from the acetonitrile ground meat extraction injected. Chromatogram B: Propoxur standards 100, 50, 20, and 10 ng injected. Chromatogram C: 90 mL of hexane-washed acetonitrile beef extract, concentrated and adsorbed on Hydromatrix, SFE with CO_2, eluted from ODS trap with 1.5 mL of acetonitrile; represents an injection 60 times more concentrated than that used for chromatogram A. Recovery of 95% propoxur based on a 30-g meat equivalent injected.

conditions of minimal ventilation. Ten grams of propoxur was first placed into a glass Petri dish and then transferred into the bottom of a glass desiccator and covered with a wire-mesh screen. After the sealed glass desiccator was equilibrated for 2 weeks, a 90-g frozen ground beef patty in a second Petri dish was placed on the screen and held in the covered desiccator for 4 h. The ground beef was extracted with acetonitrile and a 135-mL aliquot of the hexane-washed filtrate concentrated under vacuum and adsorbed on Hydromatix for SFE. Using HPLC fluorescence, 0.15 μg of propoxur was found to be present in the aliquot, i.e. approximately 0.0033 mg/kg or 3.3 ppb in the ground beef. The vapor pressure at 20 °C for propoxur of $<10^{-5}$ mbar is less than that for diazinon (1.4×10^{-4} mbar). Therefore, the low amount of propoxur vapor sorbed was as expected when compared with the higher values obtained for diazinon sorption by various agricultural materials in enclosed systems (Argauer and Cantelo, 1985).

Effect of SFE on GC/ITMS. A 3-mL aliquot of the hexane-washed filtrate from the acetonitrile pre-extraction, representing 1 g of meat, was sorbed on Hydromatrix. It was then extracted with supercritical carbon dioxide, and the propoxur and coextractives were eluted

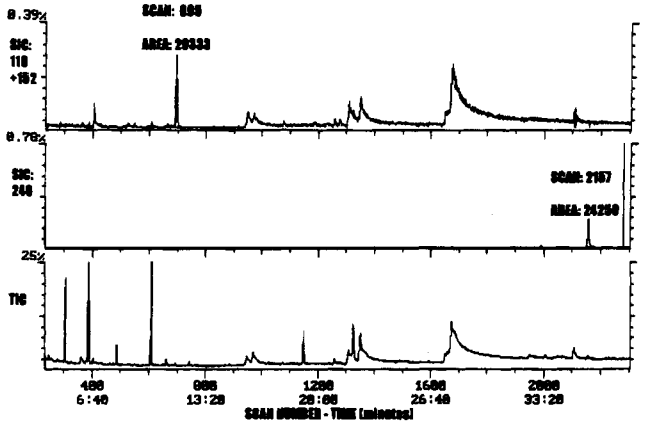

Figure 3. GC/ITMS total ion chromatograms of SFE meat extracts eluted from ODS with acetonitrile. The peak area, represented by its center at scan 695, in the selected ion chromatogram for propoxur, divided by area represented by peak 2157 for the internal standard chrysene-d_{12}, was used for quantitation.

from the trap with 1.5 mL of acetonitrile into a glass vial. Internal standard was then added. One-microliter aliquots were taken from the vial and injected into the GC/ITMS. Figure 3 presents the total ion chromatogram and the selected ion chromatograms of propoxur and chrysene-d_{12} for the SFE extracts of meat fortified at 0.1 μg/g with propoxur prior to pre-extraction. The ratio between the peak areas in the selected ion mode for propoxur and chrysene-d_{12} was obtained. Using the instrument's internal software, they were compared to the three ratios obtained for 50, 100, and 200 ppb of propoxur and for 100 ppb of chrysene-d_{12} to calculate the concentration of propoxur in the sample. On the basis of the amount detected, the recovery of propoxur was 85%.

At equivalent concentrations, the GC/ion trap signal to noise ratio for carbaryl was somewhat higher, and for carbofuran somewhat lower, than that for propoxur. Aldicarb, methomyl, and 3-hydroxycarbofuran ratios were 80, 20, and 8 times lower. The latter three carbamates are known to be thermally labile upon gas chromatography and are not detected intact by ion trap technology.

Sample Size for Analysis by GC/ITMS. On the basis of data in Table 1 on the amount of coextractives expected to be present in 1.5 mL of acetonitrile after SFE, the 1-μL injection in the GC/ITMS represented less than 0.67 g of equivalent meat sample injected. No detailed study was made to determine lifetime of the column in the presence of multiple injections of various concentrations of monoglycerides and other unidentified coextractives. It is known that glycerides autocatalytically hydrolyze and oxidize, forming aldehydes of differing molecular weights depending on the degree of unsaturation. Repetitive injections of meat sample extracts are expected to contaminate the GC capillary column, producing anomalous ion trap peaks, some of which are evident in Figure 3. We are investigating other packing material such as an aminopropyl bonded silica sorbent to replace the Hypersil ODS in the solid phase sorbent trap into which the carbon dioxide is decompressed after extraction. Then, by proper selection of the eluting solvent, more of the coextractives can be selectively retained on the solid phase, concentrating the pesticide in the eluate.

Need for Pre-extraction of Meat Sample Prior to SFE. Certainly it would be highly desirable to be able to use a smaller sample of ground meat, eliminate the acetonitrile pre-extraction, and go directly to the supercritical fluid extraction step. Because of the instrumental constraints of the system Model 7680T SFE module used, and the size of the solid phase sorbent trap contained therein, for a 3-g sample of ground meat containing about 20% fat, approximately 600 mg of lipid, mainly as the triglycerides, would be transferred, completely clogging the trap (refer to monostearin, Table 1). Even if the trap were to be increased in size, the resulting mixture of triglycerides, carbamates, and other coextractants would require additional cleanup.

Relationship between Methods and Tolerance Levels in Meat. Tolerances have been established for the combined residues of the insecticide carbofuran and its metabolites in cattle meat at 0.05 ppm, for aldicarb at 0.01 ppm, and for carbaryl at 0.1 ppm. Since no tolerances for propoxur and other carbamate insecticides have been established in meat, no residues are permitted (*Code of Federal Regulations*, 1992).

Conclusions. Pre-extraction of ground meat samples with acetonitrile removes a substantial amount of the matrix, concentrates polar insecticides, and permits large sample sizes, thus assuring a representative sampling prior to SFE. The size of aliquots from the acetonitrile pre-extraction is selected for SFE on the basis of the sensitivity required and the amount of coextractives present that may cause contamination of the GC column.

GC/ITMS detects propoxur in the SFE extracts at picogram injection levels, corresponding to 1–100 ppb in the meat sample. Limits of detection depend on the size of the sample and the degree of cleanup required. This research should benefit regulatory agencies by providing rapid quantitation of samples containing pesticides and increasing the number monitored. This will help assure a safe food supply and improve the quality of our environment.

Pre-extraction of agricultural commodities with acetonitrile prior to SFE and instrumental detection, which is known to remove plant waxes, should be useful for determining acetonitrile-soluble pesticides and drugs in meat, agricultural produce, and processed foods.

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