PESTICIDE AND INDUSTRIAL CHEMICAL RESIDUES

Enhanced Supercritical Fluid Carbon Dioxide Extraction of Pesticides from Foods using Pelletized Diatomaceous Earth

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Supercritical fluid carbon dioxide (SC-CO_2), when used with an extraction enhancer, comprises a supercritical fluid extraction (SFE) system for extraction of pesticides and matrix components from fatty and nonfatty foods. After being mixed with the enhancer, samples ranging from 95% water to pure lipophilic oils can be extracted efficiently with SC-CO_2. This extraction technique yields analyte recoveries in excess of 85% for over 30 types of pesticides at incurred levels ranging from 0.005 to 2 ppm in such diverse matrixes as carrots, lettuce, peanut butter, hamburger, and fortified butter fat and fortified potatoes. SC-CO_2 provides a solvent medium that is nontoxic, nonflammable, and inexpensive while also eliminating the use and disposal of potentially carcinogenic organic solvents.

The Total Diet Study of the U.S. Food and Drug Administration (1, 2) monitors pesticide residues in 234 table-ready food items 5 times a year. Results from this study are used as a reference in setting regulatory tolerances and in determining daily pesticide intake for people of different ages.

Analytical methodologies found in the *Pesticide Analytical Manual*, Vol. 1 (*PAM I*) (3) for this program use significant quantities of organic solvents during extraction for each series of items. The cost and the disposal expense for organic solvents has prompted our laboratories to evaluate alternative extraction procedures such as supercritical fluid extraction (SFE).

Supercritical fluid extraction (4) is a technique to extract analytes from sample matrixes using dense gases. Supercritical fluid carbon dioxide (SC-CO_2) is by far the most widely used extraction medium for SFE because it is nontoxic, nonflammable, and facilitates extraction at low temperatures in a nonoxidizing environment. Carbon dioxide (CO_2) becomes a supercritical fluid when it is operated above its critical pressure (1070 psi) and critical temperature (31°C).

Several references in the literature document the solubility of pesticides in compressed CO_2. Such studies range from engineering-scale extractions (5) to removal of pesticides from natural products extracted with SC-CO_2 (6). A number of studies have been published recently describing extraction of pesticides from such diverse matrixes as soils (7–9), plant tissue (10), and fish (11). Supercritical fluid chromatographic research has also demonstrated that a variety of pesticides can be separated using SC-CO_2 eluents (12, 13).

The SC-CO_2 extraction system developed by King et al. (14) exhibits the capabilities needed for extracting the food items in the Total Diet Study monitoring program. This system is ideal for trace (≥0.001 ppm) pesticide residue analysis because pesticide residues and lipids can be extracted from large samples efficiently. In addition, this system was used by Favati et al. (15) to extract carotene from alfalfa leaf protein concentrates. These studies also show that >10% water in the sample interferes with SC-CO_2 extraction of the lipids from many sample types. Complete extraction of lipids was achieved after dehydrating the sample at 50°C. Dehydration is also possible with freeze drying; however, such equipment is expensive. Both dehydration techniques are time consuming and increase the possibility of the loss of volatile analytes.

The present paper describes an alternative method for enhancing SC-CO_2 extraction of analytes and lipids from sample matrixes in the presence of water. Enhanced SC-CO_2 extraction is achieved after mixing the sample with pelletized diatomaceous earth, which disperses the sample material and adsorbs water.

METHOD

Principle

Mix fatty and nonfatty samples with the extraction enhancer and load into extraction tube. Extract samples with SC-CO_2 and collect residues. Collect fatty sample extracts in a round bottom flask. Clean up a portion of this residue with gel permeation chromatography (16) and Florisil adsorption chromatography (17). Determine organochlorine residues by gas chromatography (GC) using an electron capture detector (ECD) and an electrolytic conductivity detector in the halogen mode (HECD). Trap nonfat extracts on Florisil packed in a stainless steel column. Elute nonfat extracts from Florisil trap with acetone and analyze by GC for organophosphate residues using a flame photometric detector (FPD) in the phosphorus mode. If needed, clean up nonfat extracts on Florisil before determination of organochlorine pesticide residues by ECD and HECD.

Apparatus and Reagents

(a) *Extractor.*—Extractions are performed with apparatus as shown in Figure 1. CO_2 from a cylinder (A) (National Welding Supply Co., Bloomington, IL) is fed to a compressor (C) (Model AGT-62/152-C, Haskel Engineering Corp., Burbank, CA) through a check valve (CV) and 5 μm particulate filter (F). Extraction pressures are set to the desired value by adjusting the air intake valve to the compressor in tandem with the setting on the downstream micrometering valve (MV). This arrangement allows extractor pressure to be regulated to ±1.4 MPa (203 psi). Gas is admitted into the extraction tube by a series of valves (SV-1, SV-2, SV-3, SV-

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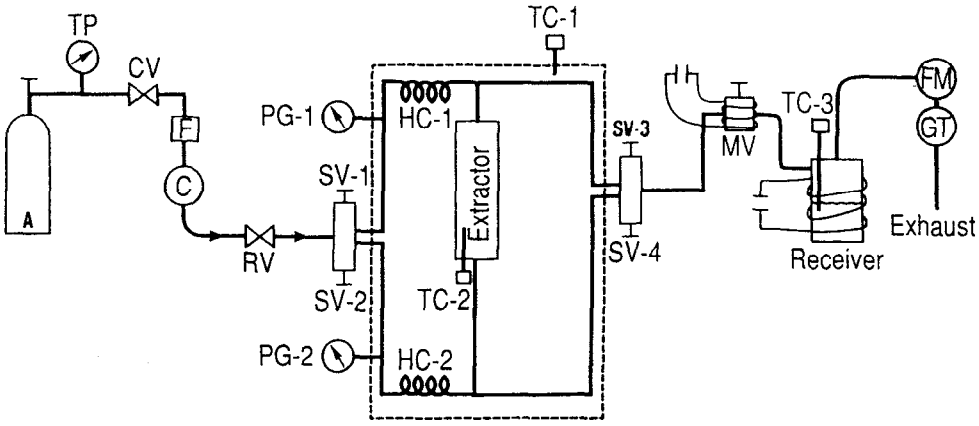

Figure 1. Supercritical fluid extraction system. Dashed lines indicate thermostated region. A = cylinder; C = compressor; CV = check valve; F = particulate filter; FM = flow meter; GT = gas totalizer; HC = equilibrating coils; MV = micrometering valve; PG = pressure gauge; RV = relief valve; SV = on-off valve; TC = thermocouple; TP = tank pressure.

4) operated at ambient temperature, which permits gas flow from either end of the extraction vessel. The extraction tube is mounted vertically in a Hewlett-Packard 7610 gas chromatograph oven. Extraction gas is equilibrated to oven temperature by passing through a 3 m coil (either HC-1 or HC-2; see Figure 1). Extractor tubes consist of 316 SS tubing (Part No. 15-009, Autoclave Engineers, Erie, PA) pressure-rated to 76 MPa (11 020 psi) at room temperature, with dimensions of 1.75 cm id × 30.5–56 cm. Interconnecting lines between the major components of the extractor consist of 316 SS, 0.32 cm od, 0.159 cm id tubing rated to 80 MPa (11 600 psi) at 93°C. Pressure gauges (PG-1, PG-2; see Figure 1) are used to monitor extraction pressure and pressure drop across the extraction tube. Oven temperature is assessed by thermocouple (TC-1); extractor tube temperature is monitored by TC-2.

The solute-laden fluid is next passed through a flow controlling micrometering valve (MV) to a receiver vessel. The sudden decompression of the SC-CO_2 creates rapid cooling of the micrometering valve. In all cases, the valve should be heated to a temperature sufficient to prevent formation of solid particulates that can plug the orifice and the attached exit line. The CO_2 and extract separate in the receiver and the gas passes through a flow meter (FM) and a gas totalizer (GT) before being vented to the atmosphere. The temperature of the receiving vessel is monitored by TC-3. Three different receiver vessels were used in this study.

(**b**) *Receiving vessel 1.*—Modified 300 mL Magnedash autoclave (Part No. 70-1395; Autoclave Engineers). The stirring assembly of the autoclave is removed, and the portals fitted with a thermocouple, a gas delivery tube to the bottom of the autoclave, and a dip tube for sampling. This vessel is held slightly above atmospheric pressure and heated to 40–50°C.

(**c**) *Receiving vessel 2.*—Consists of 2 main parts that include connecting adapters and a round-bottom flask. The exit line from the MV fits into a thermometer adapter (No. 8299-10, Ace Glass, Vineland, NJ), which is inserted into a bushing adaptor (No. 5021-09, Ace Glass). The bushing adaptor fits into a gas inlet adaptor (No. 5265-10, Ace Glass) and this assembly fits into the 24/40 joint of a heated round bottom flask, 250 mL (No. 6905-24, Ace Glass). This collection vessel is operated at ambient temperature.

(**d**) *Receiving vessel 3.*—A reducing union (Swagelok SS-810-6-4, 1/4 × 1/2 in.) connected to a stainless steel column 0.95 cm (1/2 in.) od × 30.4 cm (1 ft) with a reducing union (SS-810- 6-2, 1/2 × 1/8 in.) attached to the other end. The exit line from the MV is connected to the 1/4 × 1/2 in. reducing union with a 1/4 in. nut and graphite vespel ferrule. The stainless steel column is prefilled with 5 g activated Florisil held in with glass wool plugs. This collection vessel is operated at ambient temperature.

(**e**) *Kuderna-Danish (K-D) concentrator.*—500 mL (Kontes Cat. No. K-570025-0500).

(**f**) *Snyder column.*—Three-ball (Kontes Cat. No. K-570000).

(**g**) *Microevaporative concentrator.*—(No. 6709, Ace Glass).

(**h**) *Gel permeation chromatograph (GPC).*—Fatty sample extractants were cleaned up on an Auto-Prep 1002B equipped with a 60 × 2.5 cm id column (Analytical Biochemistry Laboratories, Inc., Columbia, MO), slurry packed with 33 g Bio-Beads SX-3 resin (200–400 mesh, Bio-Rad Laboratories, Richmond, CA) and compressed to a bed length of ca 20 cm. Eluting solvent is methylene chloride–hexane (50 + 50, v/v) pumped at a flow rate of 5 mL/min with an operating pressure range of 0.055–0.076 MPa (8–11 psi). GPC was set up with a 12 min dump, 16 min collect, and 0 min wash cycle.

(**i**) *Gas chromatograph (GC).*—Organochlorine pesticide residues were quantitated on a Model 5880 Hewlett-Packard equipped with a 30 m × 0.32 mm DB-1701, 0.25 μm film thickness fused silica column (J & W) attached to a ^{63}Ni electron capture detector and a 30 m × 0.32 mm DB-5, 0.25 μm film thickness fused silica column (J & W) attached to a Model 4420 electrolytic conductivity detector with a specially designed cell (0.005 in. solvent orifice) (O.I. Corp.). GC is set up with a direct flash vaporization inlet with a retention gap connected to a quick-seal glass splitter. Hydrogen effluent from the splitter is attached to the above columns, which are connected to a detector. Each GC run is cycled through a 2-step linear program beginning at 110°C for 1 min ramped to 190°C at 15°C/min, held for 0 min, then ramped to 270°C at 3°C/min, held for 50 min.

(**j**) *Gas chromatograph.*—Organophosphate pesticide residues were quantitated on a Varian 6000 GC that contained a 30 m × 0.53 mm DB-17, 1 μm film thickness fused silica column (J & W) attached to a flame photometric detector (FPD) in the phosphorus mode and to a direct flash vaporization inlet. Each GC run is cycled through a linear program

beginning at 150°C for 1 min then ramped to 230°C at 4°C and held for 20 min.

(**k**) *Extraction enhancer.*—Pelletized diamataceous earth. Chem Tube Hydromatrix material (Part No. CT0001, Analytichem International, Harbor City, CA) sieved with a 30 mesh sieve, to remove fines, before being mixed with the samples.

(**l**) *Florisil.*—PR grade. 60–100 mesh, calcined at 1250°F (677°C) for 3 h (Floridin Co., Berkely Springs, WV 25411). Prepare as described in *PAM I*, Section 121.3.

(**m**) *Pesticide standards.*—Prepare from 1 mg/mL stock solutions 10% acetone in isooctane. All standards obtained from the Pesticide and Industrial Chemicals Repository, U.S. Environmental Protection Agency, Research Triangle Park, NC.

(**n**) *Solvents.*—USP 95% ethanol and pesticide grade methylene chloride, *n*-hexane, diethyl ether, petroleum ether, acetonitrile, acetone, and isooctane.

(**o**) *Alumina "C".*—1 kg (02103-99, Universal Scientific Inc., Atlanta, GA).

Sample Preparation

Fatty and nonfatty food items in this study were obtained from the Total Diet Study (TDS) and grocery store. Each item was initially prepared according to recipes used by the average American household. Large quantities of each prepared item were ground or blended into a composite. Each composite represents items purchased from 3 different locations within a specific region of the United States. The United States is divided by the FDA into 7 regions that are systematically sampled.

Sample Extraction

Weigh sample (up to 26 g of a nonfatty item with 95% moisture or 50 g of a fatty item with 50% moisture) into a 500 mL beaker and mix with 13 g sieved extraction enhancer until mixture is homogenous. Add mixture to extraction column containing a glass wool plug in bottom. Tap column to settle mixture. Add an additional 11 g Hydromatrix material to original beaker and mix. Then, add Hydromatrix fraction to top of sample column and settle by tapping. This material serves to remove any sample left in the beaker and adds an excess amount of enhancer to top of column. This step helps trap any water that may migrate during extraction. Add glass wool to top of column and mark this end of column as "top" for future reference. Assemble high pressure fittings on column and place column in extraction apparatus with end designated "top" upright in extraction oven. Attach exit line to this end. Pressurize extraction apparatus to 68.9 MPa (10 000 psi) with oven temperature set at 80°C. Extract sample with SC-CO_2, which at ambient conditions is equivalent to 100 L CO_2. Set column flow rate to yield 5 L/min CO_2 at ambient conditions. Collect sample at atmospheric pressure using receiving vessel 2 or 3 as described above in the *Apparatus* section. Collect fat samples in receiver 2 and nonfat samples in receiver 3. Elute nonfat sample extractants from Florisil trap with 50 mL acetone.

Results and Discussion

The problem caused by moisture in extraction of fatty and nonfatty foods with SC-CO_2 is eliminated when samples are initially mixed with an extraction enhancer. The Hydromatrix extraction enhancer, which is pelletized diatomaceous earth, aids in dispersing sample and adsorbing water from different sample matrixes. Each sample is mixed with an appropriate amount of material in a beaker at ambient temperature thus creating a free-flowing mixture. The free-flowing mixture is created by adsorbing excess moisture into the porous material. The extraction enhancer has the capability of adsorbing twice its weight in water. Maximum sample weight that can be extracted with this SFE technique depends on the percent moisture in the sample and the size of the extraction tube.

The free-flowing mixture is easily poured into an extraction column, thus creating a homogenous permeable extraction bed. This bed can then be extracted efficiently by SC-CO_2 with minimal channeling. The moisture adsorbs on the large surface area of the diatomaceous earth pellets enhancing the interaction between the sample and the SC-CO_2.

The sample preparation described minimizes loss of volatile analytes and is quick and easy to perform. This feature is important because, after being mixed with the enhancer, samples ranging from 95% water to pure lipophilic oils can be extracted efficiently with SC-CO_2.

Extraction studies show that both incurred and fortified pesticides can be quantitatively recovered from fatty and nonfatty foods by SC-CO_2 after being mixed with the extraction enhancer.

Butter fat was fortified with organochlorine and organophosphate pesticides at 2 different levels. The 2 fortification levels were prepared by mixing 1 mL amounts of each mixed standard, prepared from stock solutions, with separate 50 g portions of butter fat. A portion of this fortified butter (10–20 g) was then mixed with extraction enhancer or dispersed on glass wool. The glass wool was placed in a slotted half-moon-shaped stainless steel insert that was inserted into the extraction tube. Each mixture was loaded into an SFE extraction tube and extracted with SC-CO_2 using the SFE system described in Figure 1 and the parameters enumerated in the sample extraction section. Fat samples extracted with SC-CO_2 were all collected in receiver vessel 2.

A known portion of fortified butter fat, fortified fat extracted by SFE from glass wool, and fortified fat extracted by SFE from the extraction enhancer were analyzed for pesticide residues using existing methods found in *PAM I*. Samples were cleaned up by gel permeation chromatography and minicolumn Florisil adsorption chromatography before being analyzed for pesticide residues by gas chromatography.

Table 1 shows that butter fat fortified with pesticides at 2 different levels can be recovered quantitatively with SC-CO_2 from the extraction enhancer and the glass wool. No pesticides were lost from the fortified butter during SC-CO_2 extraction as compared to results obtained for the fortified butter not extracted by SC-CO_2. In addition, results in Table 1 show that the extraction enhancer does not interfere with extraction of these pesticides.

A source of halogenated contamination was found during SC-CO_2 extraction of butter fat samples. The halogenated contaminant was found to be similar to weathered Aroclor 1254. The trace contaminant was eliminated when a trap containing Alumina "C" was placed between the CO_2 tank and pump. The halogenated contaminant appears to have been contributed by the CO_2 source.

A ground hamburger composite containing 41% moisture and 10.3% fat was analyzed for incurred pesticide residues using the organic solvent extraction method (*PAM*, Vol. 1, Section 211.13c) and by SC-CO_2 extraction. SC-CO_2 ex-

Table 1. Recovery of pesticides from butter fat

Pesticide	Spiking level, ppm	Recovered, %[a] Unextracted[b]	SC-CO_2 extracted from Glass wool	SC-CO_2 extracted from Extraction enhancer mixture
	Mixed standard 1			
α-BHC	0.12	88	102	95
	0.012	114	111	93
γ-BHC	0.20	84	80	85
	0.020	102	106	81
Heptachlor	0.20	92	92	85
	0.020	91	74	80
Chlorpyrifos	0.60	86	88	87
	0.060	97	90	93
Heptachlor epoxide	0.40	85	96	82
	0.040	102	117	88
cis Chlordane	0.40	83	90	81
	0.040	88	101	85
Dieldrin	0.60	87	93	84
	0.060	99	110	98
Endrin	0.60	84	90	82
	0.060	90	88	85
HCB	0.06	94	94	94
	0.006	124	100	100
p,p-Dicofol	1.00	87	86	82
	0.100	91	92	114
trans Chlordane	0.20	87	91	84
	0.020	88	89	92
trans Nonachlor	0.20	84	92	91
	0.020	91	83	92
p,p-DDT	0.60	92	89	91
	0.060	84	100	111
p,p-Methoxychlor	2.00	107	99	98
	0.200	87	112	100
	Mixed standard 2			
Penta Cl benzene	0.04	80	93	75
	0.004	79	100	70
Penta Cl thio anisole	0.08	84	89	89
	0.008	76	101	77
Penta Cl aniline	0.10	96	100	91
	0.010	90	95	95
Penta Cl anisole	0.04	91	106	87
	0.004	89	96	105
Dichloran	0.10	86	85	84
	0.010	98	90	118
Tecnazene (TCNB)	0.06	90	88	86
	0.006	80	82	89
Quintozene (PCNB)	0.08	90	93	85
	0.008	80	116	92
DCPA (Dacthal)	0.10	94	97	89
	0.010	89	111	95
Octachlor epoxide	0.20	95	103	93
	0.020	108	117	103
Endosulfan I	0.20	92	100	90
	0.020	86	97	92
p,p-DDE	0.30	90	95	95
	0.030	108	104	98
p,p-TDE	0.40	92	116	100
	0.040	92	102	92
Endosulfan II	0.40	91	111	96
	0.040	89	74	91
Endosulfan sulfate	0.40	96	107	102
	0.040	94	98	98
	Mixed standard 3			
Diazinon	0.20	80	93	80
	0.02	80	75	71
Malathion	0.60	88	100	77
	0.06	78	72	79
Methyl parathion	0.40	68	70	87
	0.04	73	73	98
Parathion	0.40	78	73	87
	0.04	84	85	90
Methyl chlorpyrifos	0.40	78	84	94
	0.04	90	85	85
Chlorpyrifos	0.40	99	99	97
	0.04	90	90	90

[a] Single determination.
[b] Fortified fat was carried through cleanup procedures without being extracted by SC-CO_2.

traction was conducted on 40 g ground hamburger mixed with extraction enhancer as well as 40 g ground hamburger previously dried overnight in a 50°C forced air oven. The dried material and mixture were loaded into separate extraction tubes and extracted with SC-CO_2. The 3 extracts were analyzed for pesticides as described above.

Table 2 shows that SC-CO_2 extraction of moist fatty samples yields sub-ppm pesticide amounts similar to those found by organic solvent extraction. This is important because it shows that a SC-CO_2 extraction of a sample mixed with extraction enhancer can be used in place of the organic solvent extraction step as well as the time-consuming sample drying step with SC-CO_2 extraction.

Peanut butter containing 52.3% fat and 1.8% moisture was analyzed for incurred pesticide residues using an organic solvent extraction (*PAM*, Vol. 1, Section 211.13c) and SC-CO_2 extraction. SC-CO_2 extraction was conducted on 20 g peanut butter mixed with 13 g extraction enhancer. Extracts were analyzed for pesticides as described above. Also, SC-CO_2 extraction of peanut butter macerated in glass wool yielded incomplete extraction because of channeling. Visual examination of the extracted glass wool bed showed that channeling was due to a nonhomogeneous extraction bed. Physical properties of the creamy peanut butter contributed to uneven distribution in the bed and, hence, to incomplete extraction. On the other hand, SC-CO_2 extraction of peanut butter mixed with the extraction enhancer resulted in complete extraction without channeling of the extraction fluid. Complete extraction was possible because the peanut butter extraction enhancer created a permeable homogenous extraction bed.

Results in Table 3 show that comparable results can be achieved for peanut butter with either extraction technique. This also shows that a high fat sample with low moisture

Table 2. SC-CO_2 extraction of incurred pesticides (ppm) in hamburger with extraction enhancer[a]

Pesticide	Original analysis, ppm[b]	Extraction enhancer mixture	Dried sample
p,p-DDE	0.0005	0.0007	0.0010
Methyl chlorpyrifos	0.0010	0.0005	0.0003
Chlorpyrifos	0.0008	0.0004	0.0003
Malathion	0.0050	0.0050	0.0028
Diazinon	0.0005	0.0005	0.0003

[a] Single determination.
[b] Conventional organic solvent extraction.

mixed with the extraction enhancer can be extracted efficiently with SC-CO_2. The fact that quintozene was not found in the SFE-extracted sample is not surprising because the quintozene peak in the original analysis may have been an interference peak.

A ground potato sample (20 g) containing 79.8% water and <0.1g fat/100 g was fortified with 40 μL of a mixed standard containing 13 pesticides. The fortified sample was mixed with the extraction enhancer and extracted with SC-CO_2. Recoveries of the fortified pesticides in the potato sample are excellent (Table 4).

High moisture nonfatty samples can be extracted easily by SC-CO_2 without first removing water. The extraction enhancer adsorbed 15.96 mL water. There was <0.2 g water in the final extract.

Lettuce (95% water, <0.1% fat) and carrots (88% water, <0.2% fat) were analyzed for incurred pesticide residues using organic solvent extraction and SC-CO_2 extraction. Acetone was used in the conventional procedure for extracting 100 g of each sample (Luke procedure, *PAM*, Vol. 1, Section 232.4). An aliquot of each sample extract equivalent to ca 20 g sample was partitioned with methylene chloride, thus extracting pesticide residues and coextractants from sample matrixes. Solvent was evaporated to a low volume in a Kuderna-Danish assembly at which time hexane was added and re-evaporated to a low volume. Samples were then cleaned up on a mini-Florisil column and analyzed for pesticide residues by gas chromatography. In addition, SC-CO_2 extraction was performed on 20 g of each sample after each was mixed with extraction enhancer. The SC-CO_2 extract was dissolved in acetone and then evaporation and cleanup as described above were performed.

With the exception of 1 analyte, all incurred pesticide residues found in the samples were confirmed in both the conventional and SC-CO_2 extracts. Table 5 shows that both extraction techniques are comparable. Methamidophos was not found in the SC-CO_2 extract of lettuce because it was irreversibly adsorbed to the Florisil trap. Methamidophos is lost when carried through the Florisil column cleanup procedure.

The present study shows that the Hydromatrix material is a viable extraction enhancer for extraction with SC-CO_2. It also allows for application of the dense gas extraction technique to a variety of substrates, such as foods, biological tissue, and fine particulate solids (clay) (18).

Table 3. SC-CO_2 extraction of incurred pesticides (ppm) in peanut butter with extraction enhancer[a]

Pesticide	Original analysis, ppm[b]	Extraction enhancer mixture
Penta Cl benzene	0.0008	0.0010
HCB	0.0004	0.0004
Penta Cl anisole	0.0007	0.0001
Quintozene	0.0004	—
Penta Cl aniline	0.0020	0.0021
Penta Cl thio anisole	0.0008	0.0002
Heptachlor epoxide	0.0006	0.0004
Dieldrin	0.0030	0.0032
Chlorpyrifos	0.0070	0.0049
p,p-DDE	0.0020	0.0021
Toxaphene	0.1200	0.0800

[a] Single determination.
[b] Conventional organic solvent extraction.

Table 4. Recovery of pesticides from potatoes using SC-CO_2 extraction with extraction enhancer

Pesticide	Spiking level, ppm	Recovered, %[a] Extraction enhancer mixture
α BHC	0.024	90
γ BHC	0.040	82
Heptachlor	0.040	85
Chlorpyrifos	0.120	97
Heptachlor epoxide	0.080	95
cis Chlordane	0.080	88
Dieldrin	0.120	98
Endrin	0.120	99
Diazinon	0.020	94
Chlorpyrifos methyl	0.040	96
Malathion	0.060	84
Ethion	0.060	92
Phosalone	0.200	95

[a] Single determination.

Table 5. SC-CO_2 extraction of incurred pesticides (ppm) in lettuce and carrots with extraction enhancer

Pesticide	Original analysis, ppm[a]	Extraction enhancer mixture
	Lettuce[b]	
Methamidophos	0.0009	None Found
Acephate	0.0040	0.0020
β Mevinphos	0.0050	0.0040
Demeton-*S*-sulfone	0.0100	0.0080
Disulfoton sulfone	0.0040	0.0030
DCPA (Dacthal)	0.0030	0.0050
p,p-DDE	0.0010	0.0050
p,p-DDT	0.0010	0.0030
	Carrots[b]	
Tecnazene (TCNB)	0.060	0.060
p,p-DDE	0.070	0.031
p,p-DDT	0.060	0.028
o,p-DDT	0.020	0.016
Linuron	0.040	0.070

[a] Conventional organic solvent extraction.
[b] Single determination.

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