Detection of Aldicarb Sulfone and Carbofuran in Fortified Meat and Liver with Commercial ELISA Kits after Rapid Extraction

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Rapid methods of extraction were developed to screen for the presence of carbofuran and aldicarb sulfone in meat and liver using commercial ELISA kits for analysis. The general extraction procedure consisted of blending the ground meat or liver with water or acetonitrile, filtering or centrifuging the extract, and then performing ELISA with commercially available kits. This procedure helped determine the insecticides fortified at concentrations near or below the regulatory tolerance levels for carbofuran and aldicarb in these matrices. Assays for aldicarb sulfone were also carried out directly in bovine milk, blood, and urine. The extraction procedure was also applied to the Enzytec biosensor ticket that is based on cholinesterase inhibition.

INTRODUCTION

The Schechter–Haller colorimetric method for measuring residues of the chlorinated insecticide DDT (Schechter et al., 1945) was used worldwide prior to the advent of electron-capture gas chromatography in the early 1960s. These methods, as well as multiresidue methodologies developed for the various classes of pesticides, require extraction followed by a "cleanup" step prior to the concentration and instrumentation steps of the particular procedure. These established methodologies have been traditionally used for monitoring pesticide levels in agricultural crops and the environment. To lower cost, speed analysis, and simplify the procedures, these methodologies are continuously being modified for the detection of pesticide residues in food and other matrices. For example, carbamate pesticides have been measured by electron-capture gas chromatography after derivatization (Argauer, 1969; Butler and McDonough, 1971; Gutenmann and Lisk, 1965) and by nitrogen-selective detection (Nelson and Cook, 1980). More recently, the combination of fluorescence detection with liquid chromatographic separation has been used to quantify carbamate pesticides in various matrices (Blaicher et al., 1980; de Kok et al., 1990; Krause, 1985; McGarvey, 1989; Moye et al., 1977).

Enzyme-linked immunosorbent assay (ELISA) and other immunochemical methods for detecting pesticides, toxic substances, and environmental pollutants have been the subject of several recent symposia, books, articles, and reviews (Fukal and Káš, 1989; Jung et al., 1989; Kaufman and Clower, 1991; Newsome, 1986; Paraf and Peltre, 1991; Vanderlaan et al., 1991; Van Emon and Mumma, 1990; Van Emon et al., 1989). Unlike the original colorimetric assay for DDT, ELISA is based on a kinetic reaction that increases sensitivity for detecting a specific analyte through enzymatic enhancement of a color or fluorescence development after an immunological equilibrium is reached.

Recently, commercial ELISA kits have become available for detecting residues of carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) and aldicarb (2-methyl-2-(methylthio)propanal O-[(methylamino)carbonyl]oxime) in water. These carbamate insecticides are used on agricultural crops to maintain food quality and reduce crop losses. The tolerance levels are 0.01 ppm for aldicarb and metabolites and 0.05 ppm for carbofuran and metabolites in the muscle, fat, milk, and meat byproducts of cattle, goats, sheep, and hogs (Code of Federal Reg-ulations, 1991). By following the label recommendations for the proper use of these insecticides, the farmer and the consumer are assured that tolerance levels are not exceeded. However, residues may occur because of accidental or deliberate adulteration.

The objectives of this research were to (1) investigate the use of commercial ELISA kits as rapid detection systems for pesticides in complex matrices near tolerance levels and (2) develop a method of rapid extraction amenable to other detection technologies foregoing cleanup, concentration steps, and, where feasible, use of organic extraction solvents. Matrices studied included ground beef, milk, blood, urine, canned cat food, and pig and chicken livers.

MATERIALS AND METHODS

Standards. Analytical reference carbofuran (99.5% purity) and aldicarb sulfone (99.0% purity) were obtained from the EPA Analytical Chemistry Laboratory, Beltsville, MD. Analytical standards of 100 mg/L were prepared in deionized water for aldicarb sulfone and in HPLC-grade methanol for carbofuran and stored in the refrigerator. Standards in water for the ELISA procedures were provided with the ELISA kits and compared with the solutions prepared from water dilutions of the 100 ppm standards in each analysis. Fortification solutions were also made from water dilutions of the 100 ppm standards. HPLC was used to monitor the stability of the carbofuran standards. Dilutions of carbofuran standards in water photodecomposed over several days, requiring fresh standards to be made before each analysis. Aldicarb sulfone remained stable in water over several weeks. The solubility of carbofuran and aldicarb in water at 25 °C is 700 and 6000 ppm, respectively, making them suitable for extraction with water and analysis by ELISA.

Samples. Ground beef, ground chuck, chicken livers, milk, and canned cat food samples were purchased from a local supermarket for analysis. These samples were assumed to contain no aldicarb or carbofuran residues. Pasteurized and homogenized vitamin D whole and 2%-fat milk samples were tested with no significant differences in the ELISA results. According to the manufacturer's label, the cat food contained meat byproducts, poultry byproducts, liver, fish, fish byproducts, wheat flour, soy flour, and chemical additives. Pig liver, cow blood, and cow urine samples were obtained through the Meat Science and Dairy Science Laboratories (USDA, ARS, Beltsville, MD) from animals that were not exposed to pesticides. The blood was centrifuged soon after collection to separate the clotted material from serum which served as the sample.

Carbofuran Extraction. The procedure for extracting carbofuran from ground chuck, cat food, and pig and chicken

livers consisted of blending 20 g of sample with 100 mL of water for approximately 1 min. The liver samples were blended to improve sample homogeneity before weighing and blending with water. The ground meat extracts were filtered through Whatman 113V filter paper, and the liver samples were centrifuged; the cat food extracts were decanted to separate the water from the blended solid. The extracts were then analyzed by ELISA. Samples were fortified at various levels of carbofuran by adding the fortification solution directly to the samples in the blender. To determine the loss of analyte in the extraction, aliquots of blank extracts were fortified prior to analysis.

Carbofuran was also extracted from fortified ground chuck with acetonitrile, and the results were compared with the water extraction. The same procedure was followed as in the case of water extraction except that 10-mL volumes of the filtered acetonitrile extracts were pipetted into vials and evaporated to dryness using a vacuum centrifugation evaporator (Savant Speedvac 200 with RT4104 refrigerated trap and VP190 pump; Farmingdale, NY). Then, another 10 mL of water was pipetted into the vials to reconstitute the solutions for immunoassay.

Carbofuran ELISA. The EnviroGard carbofuran ELISA test kit (Millipore, Bedford, MA) was used for analysis of the samples. The procedure in the information packet enclosed with the kit was followed. Briefly, 160 μL of sample and 4 drops (160 μL) of carbofuran enzyme conjugate solution were added to each antibody-coated test tube and incubated for 5 min. The tubes were then rinsed three times with water, and after shaking the tubes dry, 4 drops each of substrate and chromogen solution were added. After 5 min, a drop of stop solution and 500 μL of water were added to each tube. A portable tube-reading photometer (Ohmicron Model RPA-III; Newtown, PA) fitted with a 450-nm optical filter was used to measure the absorbance of each tube.

Aldicarb Sulfone Extraction from Meat. The procedures were the same as for the carbofuran extraction with acetonitrile from meat. The fortification solution was added to the meat directly before extraction, and control fortifications were made before evaporation and before analysis to determine losses in previous steps.

Aldicarb Sulfone Analysis in Liquid Matrices. Blank and 10 ppb aldicarb-sulfone-fortified milk, blood, and urine samples were analyzed directly and after 2× and 10× dilutions with water. Thus, concentrations of the fortified samples for ELISA were 10, 5, and 1 ppb of aldicarb sulfone in pure, 50%, and 10% solutions, respectively.

Aldicarb ELISA. EnviroGard aldicarb ELISA plate kits from Millipore were used for analysis of the samples. The procedure described in the information packet enclosed with the kit was followed. Unlike the carbofuran tube kit, the antibody for aldicarb was attached to microtiter wells which called for 80-μL sample volumes in triplicate wells and incubation with an equal volume of the aldicarb enzyme conjugate solution (2 drops) for 1 h. Also, the substrate/chromogen solution was allowed to stand for 30 min before the stop solution was added. A Molecular Devices Thermomax plate reader (Menlo Park, CA) was used to measure the absorbance of the wells at 450 nm. The ELISA data were quantified in terms of % Bo, which is the absorbance of the sample divided by the absorbance of the water blank. Absorbance and % Bo in ELISA are inversely proportional with analyte concentration, and a linear response is obtained when the signal is plotted versus the log of concentration. When comparing results between analyses, % Bo gives more consistent values than absorbance measurements because deviations among separate assays are normalized.

Cholinesterase Inhibition. The following procedure was found satisfactory for ground beef fortified at the tolerance level of 0.05 ppm. Fortification was accomplished by adding 25 μL of a 100 μg/mL carbofuran standard in methylene chloride to 50 g of ground beef. A sample of 50 g of ground beef was blended with 200 mL of water for 1 min and filtered to remove the fat and fiber. A 150-mL portion of the extract was transferred to a separatory funnel and extracted with 100 mL of methylene chloride. The lower gel-like layer was transferred to an Erlenmeyer flask and 60 g of anhydrous sodium sulfate added. A 50-mL portion of the recovered methylene chloride was decanted into a flask and concentrated under vacuum to 3 mL. This
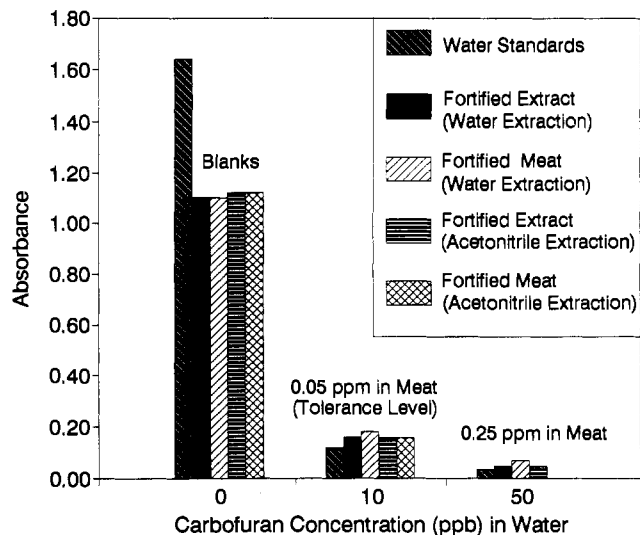

Figure 1. Carbofuran in ground chuck determined by ELISA after extraction with water and acetonitrile. Fortified extract refers to blank extracts fortified prior to assay. The difference between the absorbances in the fortified extract and the fortified meat samples corresponds to the carbofuran lost in the blending and filtration steps of the extraction. The extraction of 20 g of meat at 0.05 ppm with 100 mL of water approximates a carbofuran concentration of 10 ppb in the water extract.

concentration ratio allowed the detection response of a ticket to correspond to the tolerance level of carbofuran in meat. For detection, an EnzyTec ticket was removed from the packet and half of the foil was removed to expose the white disk. A 30-μL aliquot of the methylene chloride concentrate was added to the disk slowly, allowing the solvent to evaporate. Then, 3 drops of distilled water was added to the disk. Two minutes later, the foil was removed to expose the second disk, the ticket was folded at the perforation, and the disks were pressed together and held in hand for 3 min. A blue color indicated that a cholinesterase-inhibiting pesticide was not present or was present below the tolerance level of carbofuran. A white color indicated that pesticides may be present at levels sufficient to inhibit the enzyme, and the resultant color does not form.

RESULTS AND DISCUSSION

Carbofuran in Meat. Figure 1 gives the results for the water and acetonitrile extractions of carbofuran from meat at different fortification levels compared with water standards. The figure also includes the differences in absorbances between extracts fortified just before analysis and extracted fortified meat samples. Comparison of the extracts gives an indication of the analyte losses due to binding with meat, glass, or filter paper during the blending and filtration steps, and as the figure shows, recoveries were nearly 100% with both water and acetonitrile extraction. Although a slightly lower recovery occurred when water was used for extraction, the need for a time-consuming acetonitrile evaporation step was eliminated for screening applications.

Both Figures 1 and 2 were plotted in absorbance units to give the actual values obtained. Figure 1 shows an almost 50% difference between the absorbance obtained for water and those for the meat extracts when no carbofuran is present (blanks). The differences in absorbance between the water standards and the meat sample may be caused by interferences such as proteins in the matrix. Polyclonal antibodies are known to be cross-reactive with proteins which were conjugated to the analyte during the antibody production. Though the assay was more sensitive for detecting carbofuran in water than in meat, the test readily differentiates the fortified meat
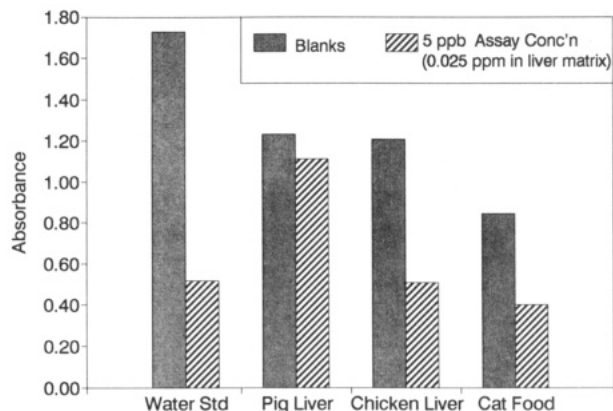
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Figure 2. Carbofuran in liver and processed cat food extracted with water and determined by ELISA. The 0.025 ppm fortification level is half of the tolerance level in meat. Liver (20 g) fortified with 0.5 μg of carbofuran (0.025 ppm) corresponds to 5 ppb in the extract (100 mL) when the aqueous content of the liver itself is ignored.
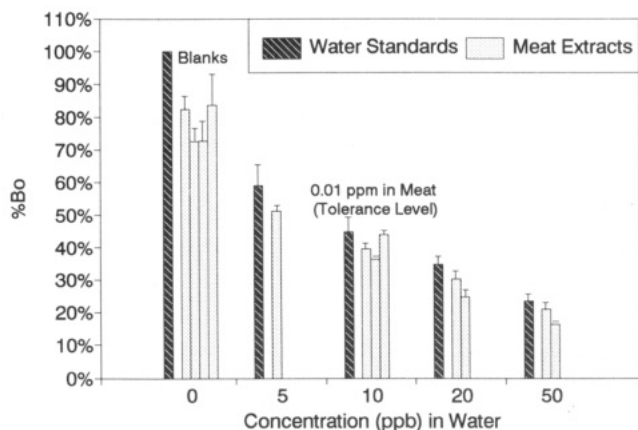

Figure 3. Aldicarb sulfone in ground beef determined by ELISA after extraction with acetonitrile. The error bars of the meat data are the standard deviations of triplicate assays of the same sample. The water standards data reflect averages and standard deviations of five assays of the same solutions (in triplicate) on different days.

samples from the blanks. The assay appeared sensitive enough to distinguish carbofuran at levels as low as 0.01 ppm in a complex meat matrix.

Carbofuran in Liver. Figure 2 presents the results of the water extracts of liver and cat food fortified with carbofuran. At a fortification level of 0.025 ppm (half of the tolerance level), the assay appears applicable to chicken liver and processed cat food but not applicable to fresh pig liver. Enzymes in the fresh liver may have decomposed the carbofuran, accounting for the losses observed.

Figures 1 and 2 show a pronounced inhibition in the ELISA compared with deionized water undoubtedly due to the complex matrices. In Figure 2, the fortification level of carbofuran was half of the tolerance concentration and yet the fortified samples could still be distinguished from the blanks (except for pig liver). Since the tolerance level is much higher for carbofuran than is the detection limit of the assay, the kits are capable of detecting carbofuran at the tolerance level using the extraction procedures outlined above.

Aldicarb Sulfone in Meat. Figure 3 gives the results of assays performed for aldicarb sulfone in ground beef. The results were reported in terms of %Bo because the data were from different assays. Unlike the carbofuran results, the meat %Bo values were always lower than the values of the standards in water which means that the

Table I. Effect of Percent Acetonitrile in Water on the Aldicarb ELISA[a]

acetonitrile (%)	absorbance (nm)	acetonitrile (%)	absorbance (nm)
0.0	1.124 ± 0.035	1.0	1.094 ± 0.038
0.1	1.246 ± 0.012	10.0	0.395 ± 0.024

[a] Standard deviations are based on absorbances of the same sample from three different ELISA plate wells.
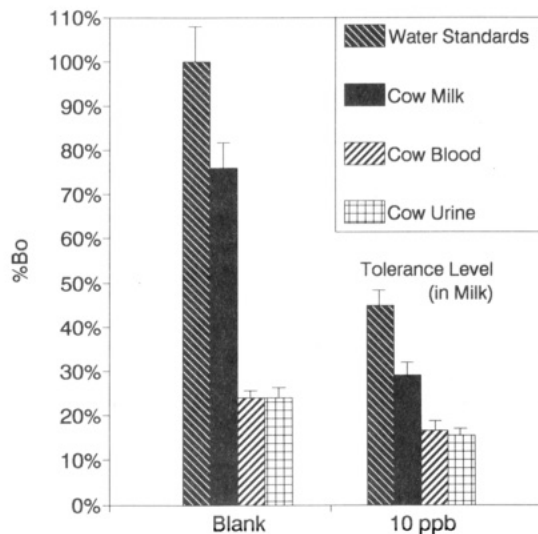

Figure 4. Direct ELISA of aldicarb sulfone in bovine milk, blood, and urine fortified at the aldicarb tolerance level for milk compared with that of water standards.

meat background of aldicarb ELISA was constant and did not significantly affect the sensitivity (slope) of the ELISA. The average percent relative standard deviations (%RSDs) of %Bo from five different analyses of the water standards were 9.4% (the water blank is by definition 100% in each assay) and 12% for three different meat extractions. In the individual assays of the samples in triplicate, %RSDs of the results were typically 5%. In a study concerning the metabolism of Temik (aldicarb) in lactating cows (Dorough, 1970), 92% of aldicarb metabolites containing C-14 in cows was excreted in the urine and 1% appeared in the milk. Aldicarb sulfone was the principal carbamate metabolite, constituting 15–19% of the radioactive products present (aldicarb sulfoxide was 4–5% and the remaining 75% of metabolites were nitriles and oximes).

Effect of Acetonitrile on ELISA. Because of the potential presence of acetonitrile after the evaporation step, the effect of acetonitrile on the results of the aldicarb ELISA was determined. Table I lists the effect on absorbance of up to 10% (v/v) acetonitrile in water. Up to 1% of acetonitrile can be tolerated without significantly affecting the aldicarb assay. ELISA kits for alachlor tolerate up to 10% acetonitrile, permitting water dilution rather than evaporation.

Aldicarb Sulfone in Milk, Blood, and Urine. Figure 4 gives the results obtained for the direct immunoassay of aldicarb sulfone in bovine milk, blood, and urine fortified at the aldicarb tolerance level for milk (0.01 ppm). The results of the water standards were included to compare with the sample results. The 20% values obtained for the unfortified urine and blood samples indicate substantial interference with the ELISA, but the fortified sample and blank can still be distinguished. These data, however, are of only limited value since only a single cow was used and the variability from samples taken from different cows may be large. In a separate study of the EnviroGard alachlor ELISA plate kit, the %RSD of seven milk blanks

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Table II. Loss of Detection Capability due to Sample Dilution in Different Matrices

matrix	difference[a] in % Bo between blank and sample (%)		
	undilted	2× dilution	10× dilution
cow milk	61.8 ± 9.9	49.6 ± 12.0	17.2 ± 10.2
cow blood	31.5 ± 11.5	38.8 ± 8.1	19.2 ± 9.6
cow urine	35.3 ± 11.6	33.2 ± 9.4	24.0 ± 8.3
water	55.2 ± 9.8	38.9 ± 10.1	18.6 ± 10.0

[a] Percent difference is ($\% Bo_{blank} - \% Bo_{sample}$)/ $\% Bo_{blank}$. Standard deviations are based on the measurements of three wells of the same sample. Aldicarb sulfone concentration was 10 ppb in the undiluted sample.

from seven different cows was 15% and for urine, the %RSD was 18%. This sample-to-sample variability over a course of time must be determined for the aldicarb kit before it can be determined if the direct ELISA approach suits the requirements for screening analysis in these matrices.

Effect of Dilution. Fortified and unfortified milk, blood, and urine samples were assayed directly and after 2× and 10× dilutions with water. Table II lists the effect of these dilutions. On the basis of the %RSDs of the percent differences of the fortified sample from the blank, the best detection strategy in the cases of milk and water is to perform the assay in undiluted solution. In the case of blood and urine, nothing is gained through sample dilution. This is due to the greater variability in the absorbance values at lower analyte concentrations than at higher concentrations. Essentially, there is no change in the %RSDs of the ELISA results at high or low concentrations. However, when measuring the difference of a blank and diluted sample, the %RSD of the result increases as the percent difference decreases. Thus, the attempt to decrease the effect of background interference by dilution proved counterproductive because of the lower detectability of the analyte at the diluted concentrations.

Matrix Interferences. In all cases studied, a substantial difference in the signal of the water blank and matrix blanks was observed. The cause of the inhibition by the matrices is unknown but could be related to a variety of factors such as pH and the presence of particle matter and chemical interferents. As long as the matrix effect is relatively constant from one sample of the same matrix to another, the ELISA technique can be applied for screening analysis. More samples must be analyzed to create an adequate data set for statistical analysis to determine a threshold response at which the occurrence of false negatives and positives is acceptable for regulatory use. The USDA Food Safety and Inspection Service has published information on the conditions necessary for approval of a new testing method (Crawford, 1989).

An additional consideration in the quantification of the ELISA results is that the sensitivity of the analyte in water is typically greater than the sensitivity of the analyte in a different matrix. It is therefore invalid to make quantitative assessments of the presence of pesticides in one matrix (*e.g.*, milk) from calibration in another (*e.g.*, water). For this reason, the ELISA approach appears more suitable as a screening tool in complex matrices rather than as an analytical method. However, matrix standards could be prepared to counteract this problem if matrix blanks are available.

Extraction Volume versus ELISA Kit Sensitivity. For the assays, sample volumes of less than 250 μL were required. Because of the sensitivities of the kits and the tolerance levels of the insecticides studied, a 20-g representative food sample can easily be blended with 100 mL of water, providing a resource for many analyses. Various

amounts of water could be used for extraction depending on the ability of a specific kit to detect an analyte.

Application to Cholinesterase Inhibition. The aqueous extraction procedure, developed for the ELISA, conveniently removes both fat and fiber while extracting the pesticide and can be applied to other biosensing methodologies. One such biosensor is the EnzyTec Biosensor Pesticide Detector Ticket (EnzyTec, Inc., Kansas City, MO) developed by Midwest Research Institute for the U.S. Army and used as a screen for detecting cholinesterase-inhibiting insecticides. The EnzyTec ticket is made of plastic and holds two disks that contain all the reagents necessary to perform a cholinesterase-inhibition color test using indoxylacetate as the substrate. Since the ticket was less sensitive than the ELISA for detecting carbofuran, a 20-fold concentration step was required for detection at the 0.05 ppm tolerance level in meat.

CONCLUSIONS

A rapid method of extraction and analysis was developed for screening trace amounts of carbofuran and aldicarb sulfone in meat and other matrices. The final extract should be in aqueous solution, requiring solvent exchange when water is not the extraction solvent. The extraction procedure may prove applicable to other polar chemicals possessing similar water solubilities. For milk analysis, no extraction was required. The presence of metabolites, matrix interferences, and other chemical residues and their effects on ELISA should be investigated to determine their effects on the results. The future development of commercial ELISA kits with a response specific for a group of pesticides such as the carbamates should provide useful pesticide multiresidue screens. This research should benefit regulatory agencies by providing alternate screening procedures that minimize the use of organic solvents and increase the number of samples that can be monitored.

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