PESTICIDE RESIDUES

Technical Bulletin

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Pesticides are either synthetic or naturally derived chemical compounds specifically developed to control a wide variety of pests, whether they be weeds, insects, molds, fungi, or rodents. They are used primarily to increase the production of food, forage, and fiber and to facilitate modern agricultural practices. By the very nature of their use in the control of insects, molds and fungi, weeds and rodents, they become common contaminants of the environment, of food and water, and of domestic structures. Pesticides are generally applied for the control of target organisms; however, non-target organisms, including humans, can be affected. Thus, to control undesirable toxic side effects and at the same time derive the benefits that can be obtained by their use, considerable regulation has been, and continues to be established regarding their proper use and resulting residues. In order to effectively regulate pesticide use, accurate and sound residue data are needed regarding the presence and quantity of pesticide residues in the food supply. Effective analytical methods are required to supply this data.

CLASSES OF PESTICIDES

Organochlorine Insecticides

Chlorinated hydrocarbon insecticides include DDT, methoxychlor, chlordane, heptachlor, aldrin, dieldrin, endrin, toxaphene, mirex, kepone and lindane along with many others. The compounds exhibit an acute effect upon insects by interfering with the transmission of nerve impulses along the axon membrane potassium and sodium channels.

From the 1940's through the 1960's chlorinated hydrocarbons were used for primary control of mosquitoes under the WHO malarial disease control program. Most organochlorine insecticides have an extremely slow rate of biodegradation, which results in a long persistence in the environment and has the effect of entering the food chain via bioaccumulation. Because of this, most of these compounds have been phased out and replaced by biodegradable insecticides. Some developing third world countries still continue to allow their use in agriculture. Methoxychlor and Toxaphene, two organochlorine insecticides with low relative persistence, are still widely used.

Organophosphate Insecticides

Organophosphates are phosphoric acid or thiophosphoric acid esters of an organic parent compound. Developed early in the 1940's these compounds exhibited excellent insecticidal properties and were quickly put into widespread use, led by the introduction of parathion in 1944. These compounds became a direct replacement for nicotine for controlling aphids and other cereal insects. Because of parathion's high mammalian toxicity, it has been replaced with other, less hazardous compounds that are widely used for a multitude of insect species. Malathion, in particular, has low mammalian toxicity compared to parathion because mammals have the capability to hydrolyze the ester, thus detoxifying the compound. This is in contrast to the insect, which does not possess this detoxification capability.

Organophosphates derive their toxicity via their inhibition of acetylcholinesterase activity of nerve tissue. Following exposure to these compounds, humans exhibit symptoms that can include tightness of the chest, lacrimation (tearing of the eyes and running of the nose), sweating, nausea, vomiting, weakness, and cramps. In an acute dose, death occurs due to respiratory failure. Organophosphates are relatively non-persistent in the environment following applications for direct control of insects on crops due to the destruction of the acid esters by hydrolysis mechanisms. Breakdown products are generally regarded as being non-toxic.

Organonitrogen Pesticides

Organonitrogens are a varied class of compounds that can produce fungicidal, herbicidal, and insecticidal control as well as plant growth regulation. Principal uses for the compounds are those with herbicidal properties. Triazines, such as atrazine and cyanazine, which are employed to optimize corn production, are the most widely used. Other compounds of interest are diuron and linuron, prometron, prometryn and diphenylamine to name a few.

Organonitrogens, because of their discreet chemical structures and numerous sub-classes produce a myriad of effects including photosynthetic inhibition, acaracide toxicity, phytotoxicity and fungicidal activities. Generally regarded as low risk compounds at residue levels, acute effects have been observed in mammals at elevated dose levels.

Carbamate Pesticides

Carbamates are a class of pesticides containing the esters of N-methyl (or occasionally N,N-dimethyl) carbamic acid. The relative toxicity of a particular Carbamate varies widely depending on its chemical structure. Principally, carbamates are insecticides and include the compounds; temik (aldicarb), carbofuran, carbaryl (sevin), methomyl, and propoxur. Dithiocarbamates on the other hand are used in fungi control.

Like the Organophosphates the Carbamates work as acetylcholinesterase inhibitors for insect control. Inhibition of enzyme activity is more rapidly reversed in mammals for carbamates compared to organophosphates.

Phenoxy Acid Herbicides

Phenoxy acid herbicides are used in the control of plants, particularly broadleaf plants, and act to kill the plant by excess stimulation of plant growth hormones. The best-known compounds in this class of herbicides include 2,4-dichlorophenoxyacetic acid, (2,4-D), 2,4-dichlorophenoxypropionic acid (dichlorprop), 2,4-dichlorophenoxybutanoic acid, (2,4-DB), and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T, dicamba, picloram and dalapon). The concern over toxicity of phenoxy acid is principally related to the presence of a co-contaminant, tetrachlorodioxin (TCDD) that is extremely toxic and can be found as a byproduct of chlorophenoxy acid manufacturing, particularly if the manufacturing process is not properly controlled.

The relative mammalian toxicities of the phenoxy acid herbicides are low. They do exhibit some water solubility, so contamination of groundwater does present a concern that warrants monitoring.

Other Pesticides

Currently, manufacturing and analytical residue technologies exist for a variety of miscellaneous groups or classes of pesticides. These classes include compounds based on sulfonylurea, pyrethrum, quaternary amine, aminophosphonic acid and other functionalities. Unfortunately these pesticide types are difficult to include in multiple residue assays and are method dependent for specific matrices. Generally these various classes are investigated on request.

Malathion Tolerances for some Food Commodities

FOOD	PPM	FOOD	PPM
Apple	8	Hops	1
Barley	8	Raisins	12
Garlic	8	Sweet Potatoes	1
Eggs	0.1	Wheat	8

ASSAY PRINCIPAL AND APPLICABILITY

Pesticides in our screen are extracted from the sample with a mixture of acetone/water, partitioned into methylene chloride/pet ether followed by extract cleanup using the appropriate solid phase extraction methods, then analyzed by Capillary Gas Chromatography and High Performance Liquid Chromatography. Positive detections from the screens representing potential residues being present are confirmed by Mass Spectroscopy (GC/MS or LC/MS). Method blanks are ran with each set to assure against potential method interferences. This method is applicable to fruits, vegetables, grains, beverages and low fat (<10%) finished products.

Lower Detection Limit	0.100ppm (0.025 for Carbamates)
Reporting Units	ppm
Information required with sample	Sample type and storage conditions

REFERENCES:

FDA Pesticide Analytical Manual (PAM) (1997) 302+E4+C5+DG1,2,5 and 401+E1+C1+DL1 (modified).
Luke, MA, et al (1981) J. Assoc. Off. Anal Chem. 64, 1187-1195
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