EMT 413

EXPERIMENTAL PESTICIDE CHEMISTRY AND RESIDUE ANALYSIS

INTRODUCTION

The term pesticide is used for all toxic chemicals used as pest control agents. They have become very popular with progressive farmers interested in obtaining high yields of crops. Large number of pesticides have been developed in recent years for the chemical control of diseases and pests which destroy crops and stored food grains worth millions of Naira every year. These substances may be sprayed as dust, granules or applied in the form of emulsion and suspension.

CLASSTFICATION OF PESTICIDES

Classification of pesticides into a particular group has not been found satisfactory as most pesticides are found to belong to one or more groups. Formerly pesticides were classified according to the target material i.e. insecticide, herbicides etc. but more recently emphasis is laid on the chemical nature of the pesticides. Thus pesticides can be classified on:

(1). Mode of

(2). Target organism

(3). Chemical nature.

PESTICIDE CLASSIFICATION ON MODE OF ACTION

These include:

a. Systemic pesticides or stomach poisons

b. Non-systemic/contact poisons or surface insecticides

c. Fumigants and

d. Repellants.

CLASSIFICATION O BASIS OF TARGET ORGANISM

Class	Target Organism	Examples
Acaricide	Mites and Ticks	Dicotol
Aigicide	Algae and aquatic plants	Calcium hypochate
Bactericide	Bacterial and bacterial Disease	Streptomycin
Avicide	Birds	Avitol
Piscicide	Sea Lamprey	Niclosamide
Fungicide	Fungi	Dichioram
Herbicide	Weeds	2,4,5 trichirophenoxy acetic acid
Insecticide	Insects	Carbaryl
Molluscicide	Molluscs & gastropods	Metaldehyde
Nematicide	Nematodes	Nemagon
Rodenticide	Rodents	Warfarin

PESTICIDE RESIDUE ANALYSIS

Pesticides particularly the organochlorines have been known to be ecologically important because of their persistence in the environment. Normally pesticides which are applied to eradicate particular pest have been known to remain in the environment after the observation

has been done in the changed or unchanged form. Such remains of pesticides which may remain in an environment for varying periods of time depending on the chemical nature of the res are known as PESTICIDE RESIDUE.

Pesticide residue is an integrated operation requiring sophisticated equipment and highly skilled manpower with good knowledge of pesticide chemistry.

The following steps are involved in pesticide residue analysis.

(i) Sample collection

(ii) Sample preparation/preservation.

(iii) Sample extraction

(iv) Sample clean up

(v) Qualitative and quantitative analysis.

EXPERIMENT I

INORGANIC FUNGICIDES (Copper Compds)

Preparation of Bordeaux Mixture Bordeaux mixture is essentially a mixture of line and copper sulphate. It is a suspension of very finely divided gelatinous particles having a light blue colour

It is prepared from a ratio 4:4:500 of CaO and water (4g of quick lime is dissolved in 400m1 water, CuSO in l00ml of water., Add the $CuSO_4$ in to the quicklime with constant stirring.

Tests for Soluble Copper

(a) To a little clear filtered liquid add potassium ferrocyanide

b) Pass H_2S through a clear filtered liquid of the bordeaux mixture

Preparation of Burgundy Mixture

It is a compound of copper sulphate and sodium carbonate which give a completely soluble precipitate. It is prepared by mixing copper sulphate, sodium carbonate (washing soda) and water in the ratio (6g of washing soda in l0ml of water and 4g of $CuSO_4$ in 400rn1 of water Both solutions are mixed with constant stirring until a ppt of ‘basic copper carbonate $CuCO_3.Cu(OH_2)$ is obtained

— Carry out test for soluble copper ions

—In addition to a portion, add NH in drops, then in excess

TEST FOR ALKALINITY

Carry out this test for both the Bordeaux and Burgundy mixtures.

Take 5ml the mixture and add about 50m1 of water and allow the mixture to disperse Make the volume to l00ml and filter. Take 25ml of the filtrate, boil for 2 minutes and filter if ne Add a drop of methyl red and titrate against 0.2M sulphuric acid.

Calculate the amount of Na_2CO_3 in l00ml and hence the % Na_2CO_3 in the mixture.

EXPERIMF'NT II

ESTIMATION OF COPPER IN FUNGICIDES

The estimation is based upon the fact that $CuSO_4$ liberates iodine quantitatively from KI which is estimated by titrating it against sodium through sulphate solution.

$2CuSO_4 + 4KI \longrightarrow Cu_2 + I_2 + K_2SO_4$

Procedure

Take 2gof the fungicide and add about l00ml of water to get a uniform suspension. Add 5m1 glacial acetric acid. Boil and then add about 5m1 of phosphate solution to precipitate any iron present. Make the volume up to 100ml and filter. Take 50m1 of the filtrate in a conical fl add an equal volume of 10% KI solution. Titrate against 0.1M $Na_2S_2O_3$ solution using starch as indicator.

Show by calculation how 1ml of N/10 $Na_2S_2O_3$ = 0.00635 Copper

Give --four examples of fungicide classifying them under systematic and non-systematic fungicide.

EXPERIMENT III

INORGANIC FUNGICIDES (Sulphur Compds)

Sulphur and its compds particularly polysulphides have proved invaluable as. fungicides and insecticides Lime sulphur is a common preparation used as fungicide It is prepared by boiling $Ca(OH)_2$ suspension with sulphur ($CaS + CaS_2O_3$ are formed)

Preparation

It is prepared in a ratio of 1:2:10 of CaO, Sulphur and water (e.g. mix 50g quicklime with a little water then make up to 100m1 Mix l00g of flowers of and stir well so as to obtain colloidal paste. Add 400rnl water and heat for another hour. Allow the mixture to stand until undisolved material has settled out Pour away the supernanant liquid and dilute the residue about 30 times in order to test for polysulphides and thiosulphate

Test for Thiosulphate

To about 25m1 of diluted suspension add l0ml of ammoniacal zinc chloride solution. (dissolve 5g of zinc water and add 5g ammonium chloride solid). Add 12.5ml NH_3 and dilute tol00ml) allow to stand for 10 minutes and filter Test the filtrate for thiosulphate Neutralize with HC1 and test with iodine solution

Test for Sulphide Sulphur

The residue left on the filter paper may be tested for suiphide sulphur by treating with HC1

Mercury Compound

Most of the compounds of mercury are highly toxic to all forms of life Mercuric chloride $HgCl_2$ has been used as a seed disinfectant and to control fungi attacking certain, species of fine grasses. Calornel Cu_2Cl_2 is also used for similar purposes but the high toxicity of mercury to higher animals' and plants has prevented its wide use.

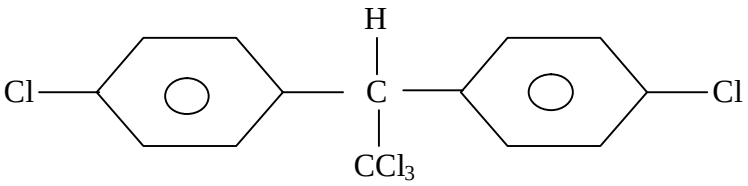
The organic mercurial compounds have of late become very popular as seed disinfectants and they have proved even superior to $CuSO_4$.

Test for Mercury

Treat a little of fungicide with Conc. nitric acid in a dish and heat to dryness Cool and add a drop of freshly prepared alcoholic solution of diphenyl carbazone. A blue colour shows the presence of mercury.

Treat the fungicide with HC1 and filter. To a portion of the filtrate add $SnC1_2$. A white precipitate turning grey shows the presence of Hg. Pass H_2S into the filtrate. A black pot of HgS insoluble in HNO_3 is produced.

EXPERIMENT IV



Pure D.D.T or 2, 2 bis (P. Chlorophenyl) 1—1—1 trichloethane is a white occurring as Long needles. Its melting point is 108.5 - 109°C and density 1.556. It is soluble in a number of organic solvents and insoluble in water. It is prepared by reacting chloral and chloro benzene in the presence of H_2SO_4.

$C1_3CCHO + 2C_6H_5Cl \longrightarrow C\ C\ H\ (C_6H_4Cl)_2 + H_2O$

The commercial product contains about 70.77% of precipitate DDT. DDT is quite stable except in the presence of alkalis' and certain metallic salts such as Al, Fe and Cr, DDT is used either in solutions of organic solvents or in the form of powder.

(i) Determination of DDT

Weigh a sample of insecticide containing 25 — 200mg (0.025 — 0.2g DDT powder) in a conical flask. Add 50m1 of a potash. Fit up a reflux condenser and reflux for 15 minutes on a water bath. Add l00ml water, cool and add 3ml HNO_3. Mix well and add 25m1 of standard Silver Nitrate Solution and shake well so as to precipitate all chloride. Add more $AgNO_3$ solution if necessary and ensure an excess of silver nitrate. Add 2m1 saturated iron-alum and 20ml of Nitric acid. Shake well and titrate excess of $AgNO_3$ with standard NH_4CNS solution until faint pink colour develops. Carry out a blank titration also in the same way.

OR after refluxinq titrate with standard HC1 solution provided

(ii) % of DDT in a Crop Sample

Weigh a known amount of the crop/seed, then crush in a mortal and digest with Nitric acid Neutralize with potassium hydroxide then follow the procedure as in (1) above

EXPERIMENT V

Extraction of Pesticide From Fish Sample

Skin the fish samples provided with a steel knife and tweezers Talcc sub—sample of muscle from the fish and homogeniseis serve as the primary sample.

Dried Formic Acid Procedure (Fort 1968)

Take 4a of the homogenised sample into a centrifuge tube, add 4ml HCOOH, place in water bath at 90°C for 30 minutes then allow to cool to room temperature. Add 4m1 Hexane shake and centrifuge for 3 minutes. Transfer the top hexane layer into a clean dry—preweighed centrifuge tube with a teat pipette Add another 4m1 Hexane and rep the extraction Also repeat the extraction by adding 4m1 of 15% diethyl ether in hexane.

The centrifuge tube was then placed in a water bath at 60°C and solvent evaporated off using a stream of nitrogen gas Cool to room temp and determine fat weight by weighing.

(b) UNEP Procedure (UNEP 1982, 1985)

Weigh, of the homogenised sample and 30g anhydrous Na_2SO_4 and blend. Transfer to a cellulose thimble (or filter paper) and insert into a S extractor. Extract with 150m1 of hexane for 4 hours, allow to cool to room temperature and evaporated on a water bath. Determine percentage fat by weighing.

EXPERIMENT VI

Analysis of Cuprous Oxide

Cuprous oxide dusting powders are used as fungicides for the control of plant diseases in Agriculture and Horticulture

Copper is determined by titration of iodine which is liberated by treating it with potassium iodide in a weakly acidic so1ution

Weigh the given sample containing 0.2g of copper and put it in a 500rnl flask Add 25m1 of water and then 5m1 of concentrated nitric acid Shake and warm a little to make it soluble. Heat it to about 5ml. Cool and add 30rnl of water and boil again for 10 minutes. Cool and add sodium carbonate till blue colour or precipitate is produced.

Add acetic acid drop by drop until the blue colour or precipitate disappear. Add approximately 2g of potassium iodide and titrate with 0.1N Sodium thiosulphate till the colour turns straw yellow. Add 5m1 of starch solution as indicator and yellow to a colourless end point.

Note

Marks will be awarded for the following:

1. A good write up on the experiment comprising of Title, Aim, Apparatus/Material Procedure, Results and Conclusion.
2. Precaution that was taken during the experiment
3. Sources of likely error and how it could be prevented
4. Calculations must be neat and straightforward
5. Practical note books must be submitted at the end of the practical class