

ELE SSAC-364

PRACTICAL MANUAL

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CERTIFICATE

This is to Certify that Shri/Ku. _____
 Enrolment No. _____ has completed all the exercises of Course No.SSAC-364
 (Agrochemicals) As per the syllabus of B.sc. Agri (Hons.) Third Year Sixth Semester in the College
 laboratory as prescribed by M.C.A.E.R./, Pune

Date: _____

Course Teacher

EXERCISE NO.1

FERTILIZER ADULTERATION TEST / IDENTIFICATION OF ADULTERATION IN FERTILIZER / DETECTION OF ADULTERATION IN FERTILIZERS [RAPID TEST]

The commonly used fertilizers are normally adulterated by either cheap fertilizer or non fertilizer substances such as sand, ash, gypsum, lime etc.

The following commonly used adulterants are used in fertilizers.

Name of fertilizers	Adulterants
1. Urea	Common salt, silica, sands
2. Diammonium phosphate (DAP)	Granular single super phosphate
3. Single super phosphate (SSP)	Sand, ash, granular gypsum.
4. Calcium ammonium nitrate (CAN)	Clay gypsum
5. Muriate of potash (MOP)	Sand common salt.
6. NPK	Single super phosphate (granular)
7. Zinc sulphate	Magnesium sulphate.
8. Copper sulphate	Sand, common salt.
9. Ferrous sulphate	Sand, common salt.

Reagents

1. NaOH (Conc.) : 40 % in water, NaOH dilute – 1 %.
2. Acetic acid : glacial
3. AgNO_3 – Dissolve 1 gm in 100 ml distilled water.
4. Cobalt nitrate : Dissolve 5 gm cobalt nitrate in 5 ml distilled water. Add 25 gm NaNO_2 and 2.5 ml glacial acetic acid. Mix and dilute to 100 ml with distilled water
5. FeCl_3 solution : Dissolve 7 gm FeCl_2 and 12 gm ammonium acetate in 1 litres of distilled water.
6. Formaldehyde : (37-40 %) Add 1 ml methanol red indicator in 100 ml formaldehyde.
7. Ammonium acetate
8. Calcium oxide (CaO)
9. Conc. And diluted acids (5 N) H_2SO_4 , HNO_3 , HCl
10. $\text{K}_3[\text{Fe}(\text{CN})_6]$ – dissolve 5 gm potassium ferricyanide in 100 ml water.

Detection of adulterants

1) Urea :

- Dissolve 1 gm sample in 5 ml water in a test tube. Add 5-6 drops of AgNO_3 . If white ppt does not appear, the sample is not adulterated with salt.
- Filter the solution, if no residue on filter paper. It is not adulterated with sand / silica.
- Heat dry urea in a test tube, if melts completely the sample is pure, if not and solid residue remains it contains adulterated with sand / silica.

2) Diammonium phosphate (DAP)

- Dissolve 1 gm powdered sample in 5 ml distilled water. Add 1 ml conc. HNO_3 and mix.
It dissolve completely, it is pure DAP. If it contains undissolved material, it is adulterated.
- To 1 gm sample add 2-3 drops of NaOH or 1 gm CaO , smell of ammonia indicates the presence of nitrogen. If not, the sample is not DAP.
- Dissolve 1 gm of sample in warm water and filter. To the filtrate add 1 ml AgNO_3 . If yellow ppt. It contains phosphate. If not, it is not DAP but SSP.

3) Muriate of potash (MoP)

Take about 1 gm sample and dissolve in 10 ml dist. Water. If sample does not dissolve completely and undissolved material settles, it is adulterated. Place powder in blue flame, which burns with yellow flame, if adulterated.

4) NPK fertilizers :

- Dissolve 1 gm of sample in 5 ml distilled water in a test tube. Add 1 ml conc. NaOH and heat place the moist (water) red litmus paper to the mouth of test tube. Paper turns blue indicates the presence of nitrogen. If paper remains unchanged, the sample does not contain nitrogen and highly adulterated.
- Dissolve 1 gm sample in 5 ml of water and filter. Add 0.5 ml of FeCl_3 , if yellow ppt. Forms which is soluble in conc. HNO_3 it indicates the presence of phosphorus.
- To the 5 ml solution of sample add 2 ml formaldehyde. The colour of solution turns red. Add NaOH drop wise till yellow colour. Add 1 ml cobalt nitrate reagent. Yellow ppt indicates the presence of potassium (Potash).

5) Potassium (potash)

Dissolve 1 gm of sample in 5 ml of water. Add 1 ml dilute NaOH and 1 ml of AgNO_3 . Yellow colour ppt indicates phosphate. If yellow ppt is not formed it is not phosphatic fertilizer.

6) Zinc sulphate :

Dissolve 1 gm sample in 5 ml water and filter. Add 8-10 drops of NaOH to the filtrate, if white ppt appears and dissolve in 10-12 drops of conc. NaOH the sample is pure. If ppt does not dissolve in conc. NaOH, it is adulterated.

7) CuSO_4 :

Dissolve 1 gm of sample in 5 ml water. The solution must be transparent blue colour. Add KSCN to the solution, if brown ppt copper is present.

8) FeSO_4 :

To the aqueous solution add 1 ml $\text{K}_3[\text{Fe}(\text{CN})_6]$, appearance of blue coloured ppt confirms iron.

Reference :

1. A.K. Gupta (2007) Practical manual of Agril. Chemistry, pp. 108-109.

EXERCISE NO.2

DETERMINATION OF [AMIDE NITROGEN] FROM UREA

Urea contains nitrogen in amide form (-NH_2) which is converted into ammonium sulphate by digesting with concentrated sulphuric acid. The NH_3 from the ammonium sulphate is liberated by adding NaOH which is distilled and absorbed in known excess standard sulphuric acid. The excess std. H_2SO_4 is titrated with std. NaOH . Nitrogen is calculated from volume of standard H_2SO_4 neutralised by ammonia factor $1 \text{ ml of N H}_2\text{SO}_4 = 0.014 \text{ g N}$.

Reagents :

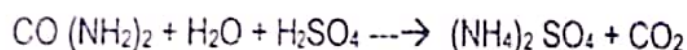
1. Concentrated H_2SO_4 (N free)
2. Salt mixture : 10 parts K_2SO_4 plus 0.5 parts CuSO_4
3. Standard H_2SO_4 (0.1 N)
4. Standard NaOH (0.1 N)
5. 40-45 % NaOH
6. Methyl red indicator (0.2% solution in 60 % alcohol)

Procedure :

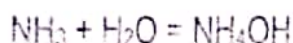
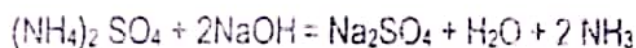
1. Take 1 g urea dissolve it in water & make up volume to 250 ml.
2. Pipette out 25 ml of the fertilizer solution in a Kjeldahl flask.
3. Add to it 25 ml of cone. H_2SO_4 slowly by sides of the flask and shake well.
4. Add about 10 g salt mixture. 5. Heat the flask initially at lower temperature and then gradually raise the temperature. Continue the digestion till the content of the flask is clear. Allow the flask to cool.
6. Distill as per the procedure given exercise NO. 9 - 10 Run a blank simultaneously without sample.

Reactions:

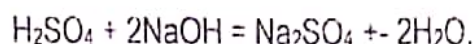
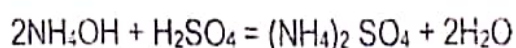
i) During digestion :



ii) During distillation



iii) During Titration :



Observation :

- | | |
|--|-----------|
| 1. Weight of urea | - W_1 g |
| 2. Vol. of urea solution prepared | - 250 ml |
| 3. Vol. of urea solution taken for nitrogen estimation | - 25 ml |
| 4. Vol. of std. H_2SO_4 taken for sample | - x ml |
| 5. Vol. of std NaOH required for titration | - y ml |
| 6. Vol. of std H_2SO_4 taken for blank | - A ml |
| 7. Vol. of std NaOH required for blank | - B ml |
| 8. Normality of std. $\text{H}_2\text{SO}_4 = 0.1$ N | |
| 9. Normality of std. NaOH = 0.1 N | |

Calculation:

1 ml of 1 N $\text{H}_2\text{SO}_4 = 0.014$ g N .

$$\% \text{ N in sample} = C \text{ ml} \times 0.014 \times \frac{\text{Vol. made}}{\text{Vol. taken}} \times \frac{100}{\text{wt. of urea}}$$

.Where C is volume of std. H_2SO_4 required for neutralising ammonia

$$C = [(X \times N) - (Y \times N)] - [(A \times N) - (B \times N)] \text{ ml}$$

Question :

1. Explain the role of the following reagents
a. CuSO_4 b. K_2SO_4 c. H_2SO_4 cone. d. 40 % NaOH .
2. Explain the principle involved in the estimation of nitrogen from urea.
3. What reactions are involved in the estimation of nitrogen ?
4. How will you know whether digestion is complete or not ?
5. What precautions will you take while carrying out distillation?

Reference book:

D.P.Motiramani and R. D. Wankhede, Laboratory manual in Agril. Chemistry PP.

EXERCISE NO.3

DETERMINATION OF AMMONICAL NITROGEN CONTENT AND NITRATE NITROGEN CONTENT FROM NITROGENOUS FERTILIZERS

Principle : The solution containing a known amount of ammonium sulphate is distilled with 40 % NaOH or 2 to 3 g MgO powder and the ammonia liberated is absorbed in a known excess std H_2SO_4 . The excess std, H_2SO_4 is titrated with std NaOH. The amount of $\text{NH}_4\text{-N}$ is calculated from amount of std. H_2SO_4 required for neutralisation of NH_3 .

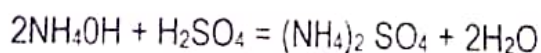
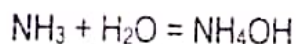
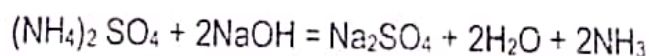
Reagents :

- 1) Std. H_2SO_4
- 2) Std. NaOH
- 3) Methyl red indicator:
- 4) 40% NaOH or MgO powder (free from MgCO_3)

Procedure :

1. Weigh One gram of a ammonium sulphate and dissolve it in distilled water & make up the volume to 250 ml.
2. Take 25 ml of solution in a distillation flask and dilute it to about 250 ml with distilled water.
3. Add 5-10 ml of 40% NaOH solution and distill as per exercise No. 9-10.
4. Run a blank simultaneously.

Reactions:



Observations:

- | | |
|--------------------------------|-----------|
| 1. Weight of ammonium sulphate | - W_1 g |
| 2. Vol. of solution prepared | - 250 ml |

3. Vol. of test solution taken for N estimation - 25 ml
4. Vol. of std. H_2SO_4 taken for sample - x ml
5. Vol. of std. NaOH required for sample - y ml
6. Vol. of std H_2SO_4 taken for blank - A ml
7. Vol. of std NaOH required for blank - B ml
8. Normality of std. Acid - 0.1 N
9. Normality of std. NaOH - 0.1 N

Calculations :

1 ml of 1 N H_2SO_4 = 0.014 g N

Volume of std. H_2SO_4 required for neutralisation of sample.

$$C = [(X \times N) - (Y \times N)] - [(A \times N) - (N \times N)] = 'C' \text{ ml}$$

$$\% \text{ N} = C \times 0.014 \times \frac{\text{Volume made}}{\text{Volume taken}} \times \frac{100}{\text{Wt. Of ammonium sulphate}}$$

$$\text{Purity \%} = \frac{\text{Estimated N \% N sample}}{\text{Theoretical N content of ammo. Sulphate (21.2 \% N)}} \times 100$$

Questions :

1. What is the additional benefit of using ammonium sulphate?
2. Explain the principle involved in the estimation of ammoniacal nitrogen from ammonium sulphate?
3. What are the reactions involved in the estimation of $\text{NH}_4\text{-N}$ from the fertilizer sample?
4. How will you calculate the purity percentage of ammonium sulphate?
5. Explain how 1 ml of 1 N H_2SO_4 = 0.014 g N.

Reference :

1. Chopra and Kanwar (1980) Analytical Agricultural Chemistry, pp. 127-128.

EXERCISE NO.4

DETERMINATION OF WATER SOLUBLE PHOSPHORUS IN SUPERPHOSPHATE [PUMBERTON METHOD]

The phosphate is precipitated as ammonium phosphomolybdate by adding ammonium molybdate. The precipitate is dissolved in a known excess of standard alkali. The excess of alkali is titrated against std. acid. From the amount of std. alkali required to dissolve the precipitate, the percent p is calculated.

Reagents :

1. Ammonium molybdate solution :- Dissolve 200 g finely ground ammonium molybdate (A.R. grade) in distilled water. If necessary heat it and add ammo hydroxide solution till the solution becomes clear and make up the volume to one litre. Now pour 9 ml of above solution into 11 ml of conc. nitric acid and shake the solution.
2. Dilute ammonium hydroxide
3. Conc. nitric acid
4. Std. NaOH (0.1 N)
5. Std. H₂SO₄ (0.1 N)
6. Ammonium nitrate (solid)
7. KNO₃ (3%)
8. Indicator-phenolphthalein (1 % in ethanol)

Procedure :

a) Preparation of water extract :

1. Weigh accurately 1.0 g of superphosphate in beaker & add hot water, stir well.
2. Filter through whatman No. 40 filter paper
3. Wash the residue with successive portion of hot distilled water and collect the filtrate in 250 ml volumetric flask.
4. Continue the washing with water till the filtrate runs free from acid (test with blue litmus paper)
5. Make up the volume upto the mark 250 ml.

b) Precipitation :

1. Pipette out 10 ml of the extract in 400 ml beaker.
2. Make the aliquot alkaline by adding amm. hydroxide and then acidic by adding conc. nitric acid (Use litmus).
3. Add 3-10 g ammonium nitrate and place the beaker on thermostat 60-65°C. On the same thermostat place ammonium molybdate reagent to attain the same temperature.
4. After 15 minutes add about 20 ml of ammonium molybdate reagent and stir slowly with the help of policeman. Canary yellow precipitate appears.
5. Again place both the beakers on their respective places. Intermittently stir the precipitate centrifugally with policeman taking care not to grind the precipitation at the interval of five minutes, continue this process for half an hour.
6. Allow the beaker to remain again for 15 minutes and test with the ammonium molybdate reagent, if precipitate appears again add more amount of the reagent.

c) Filtration :

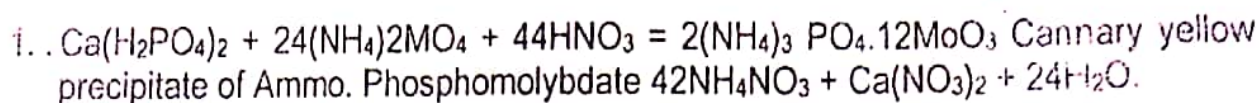
Carefully transfer the supernatant liquid on Whatman No. 40 filter paper and continue the filtration adding small quantity of 3% KNO_3 at each time allowing the liquid to drain completely before adding next portion of KNO_3 . As far as possible the precipitate should not be disturbed. Wash the precipitate till it is free from acid, (Test with phenolphthalein by taking one or two drops of alkali in a test tube dilute to 10 ml with distilled water, collect the filtrate in test tube, if pink colour persisted as such, it means precipitate is free from acid).

d) Dissolution of precipitate and titration :

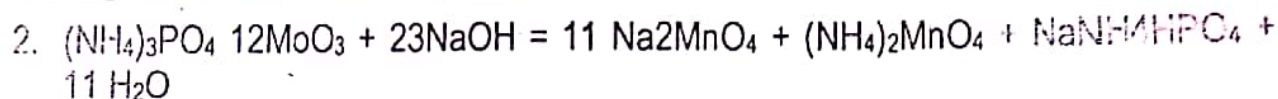
1. Carefully transfer the filter paper into the beaker in which precipitation was carried out. Then wash the sides of the beaker and funnel with distilled water.
2. Add about 50 to 100 ml of distilled water and macerate.
3. Add two or three drops of phenolphthalein indicator.
4. Add known excess standard NaOH in the beaker until the precipitate is completely dissolved as indicated by pink colour. Note the volume of alkali added.
5. Titrate the excess of alkali against std. H_2SO_4 till the content becomes colourless. Note the volume of standard acid required for titration.

Reactions :

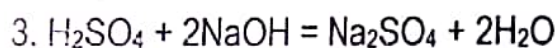
During Precipitation :



During Dissolution of precipitate :



During Titration :



Observations :

- | | |
|--|-----------|
| 1. Weight of sample | - W_1 g |
| 2. Vol. of water extract made | - ml |
| 3. Vol. of water extract taken | - ml |
| 4. Vol. of std NaOH added to dissolve the precipitate | - x ml |
| 5. Normality of std. NaOH | - 0.1 N |
| 6. Vol. of std. H_2SO_4 required for titration | - y ml |
| 7. Normality of std. H_2SO_4 | - 0.1 N |

Calculations :

Derivation of Factor :

$$1 \text{ ml of } 1 \text{ N NaOH} = 0.0031 \text{ g P}_2\text{O}_5$$

$$23 \text{ NaOH} = (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MnO}_3$$

$$46 \text{ NaOH} = 2(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MnO}_3$$

$$46 \text{ NaOH} = 2\text{P} = \text{P}_2\text{O}_5$$

$$46 \times 40 \text{ g NaOH} = 2 \times 31 \text{ P or } 142 \text{ g P}_2\text{O}_5$$

$$1000 \text{ ml } 1 \text{ N NaOH} = 1.347 \text{ g P or } 3.086 \text{ g P}_2\text{O}_5$$

$$1 \text{ ml } 1 \text{ N NaOH} = 0.0013 \text{ g P or } 0.0031 \text{ g P}_2\text{O}_5$$

$$\% \text{ P}_2\text{O}_5 = (\text{ml of NaOH} \times \text{N}) - (\text{ml H}_2\text{SO}_4 \times \text{N}) \times 0.0031 \times \frac{\text{Vol. made}}{\text{Vol. taken}} \times \frac{100}{\text{Wt. of sample}}$$

$$\% \text{ P} = \% \text{ P}_2\text{O}_5 \times 0.44$$

Questions :

1. Write the form of phosphorus present in single superphosphate.
2. Explain the role of following reagents
 - a) ammonium molybdate b) std. NaOH and std. H₂SO₄
 - c) ammo hydroxides d) KNO₃
3. Why the temperature of the precipitation medium should be 60- 70°C.
4. Explain the principle involved in the estimation of phosphorus by Pernborton method.
5. How will you judge whether the precipitation is complete?
6. Explain how 1 ml of 1 N NaOH = 0.0031 g P₂O₅

Reference book :

Chopra S.L. and J.S. Kanwar (1991) Analytical Agril.Chemistry pp. 122-124.

EXERCISE NO.5

DETERMINATION OF ACID SOLUBLE PHOSPHORUS FROM ROCK PHOSPHATE

Principle:- Phosphorus from rock phosphate is extracted by treating with conc. HNO_3 and conc. HCl . The principle of P estimation from acid extract is the same as given in the estimation of water soluble phosphorus in single superphosphate (Experiment NO. 9).

Reagents : 1) Conc. HNO_3 2) Conc. HCl 3) 0.1 N AgNO_3

All other same as expt. for the determination of WSP from SSP.

Procedure :

a) Preparation of acid extract :

1. Weigh 1.0 g rock phosphate sample and dissolve in 30 ml conc. HNO_3 and 3.5 ml of conc. HCl boil until organic matter is destroyed. Cool the solution.
2. Filter through Whatman No. 40 filter paper. Collect the filtrate in 250 ml volumetric flask.
3. Wash the residue with hot water till filtrate is free of chlorides (Test with Silver nitrate).
4. Make up the volume.

b) Precipitation :

1. Pipette out 5-10 ml of acid extract and proceed as per procedure described in Experiment No. 9

Questions :

1. Write the total per cent P_2O_5 content of rock phosphate.
2. Write the suitability of rock phosphate for its use in crop production under different soils.
3. Write other examples of water insoluble phosphate fertilizers.

Reference book :

Chopra and Kanwar (1980) Analytical Agril. Chemistry, pp. 136

A.O.A.C (1975), pp. 11

EXERCISE NO.6

DETERMINATION OF TOTAL POTASSIUM CONTENT OF NITRATE OF POTASH [BY FLAME PHOTOMETER METHOD]

Principle : The water extract of K fertilizer is atomised in the flame where the atoms of the elements are excited emitting radiations of characteristic wavelength. The radiation emitted by K atoms is passed through K filter (768 nm), which falls on photocell, emitting electrons i.e. electric current which is measured on galvanometer of flame photometer. The electric current generated is proportional to the concentration of K in the extract.

Reagents :

Standard stock solution (1000 ppm K)

Dissolve 1.2931 g KNO_3 in distilled water and make up to 500 ml.

Working solution (100 ppm K) = 10 ml of stock solution is diluted 100 ml.

Standard curve:

1. Pipette out 0, 10, 20, 40, 60, 80, 100 ml of working solution in 100 ml volumetric flasks separately and make the volume. This will be 0, 10, 20, 40, 60, 80 and 100 ppm K-solutions, respectively.

Preparation of water extract of muriate of potash

1. Weigh 0.5 g muriate of potash and dissolve in distilled water and make up the volume to 250 ml (Filter if necessary) Dilute the extract if necessary.
2. Feed the extract to the flame photometer after adjusting the scale of flame photometer with standards.

Observations :

1. wt. of sample
2. Vol. of extract made
3. Flame photometer reading

Record the standard curve readings and plot a standard curve.

Calculations :

$$\% K = \frac{\text{Graph Reading (in ppm)} \times \text{Volume made} \times \frac{1}{1000} \times \frac{1}{1000} \times \frac{100}{\text{Wt. Of sample}}}{1}$$

$$\% K_2O = \% K \times 1.20$$

NOTE: If dilution of water extract is made, introduce the dilution factor in calculations.

Questions:

1. Write the principle of flame photometry.
2. How will you prepare 100 ppm K solution of K_2SO_4 ?
3. Write the wave length of radiation emitted by K at excited state.
4. What colour of flame appear when K is burnt in flame ?

Reference book :

Chopra S.L. and J.S.Kanwar (1991) Analytical Agril. Chemistry pp. 130-133.

EXERCISE NO.7

DETERMINATION OF SULPHUR CONTENT FROM FERTILIZER [GRAVIMETRIC METHOD]

Principle

The non-sulphate inorganic S content can be converted into sulphate by oxidising with bromine, H_2O_2 or concentrate nitric acid. The sulphates can then be precipitated out with barium chloride as $BaSO_4$ which can be weighed gravimetrically by heating it at $800^\circ C$. Certain cations like Na, K, Ca, Al, Cr and Fe^{+++} cause interference which has to be removed or masked before precipitation.

Reagents

1. Concentrated Hydrochloric acid
2. Concentrated Nitric acid
3. Barium chloride 10% solution in water.
4. Silver nitrate solution 1%
5. Bromine in Carbon tetra chloride 10%

Procedure

- ♦ Accurately weight 2 gm sample in a 250 ml. beaker.
- ♦ Add 20 ml of 10% bromine solution and let it stand for 30 minutes with intermittent mixing by swirling the beaker under a fume hood.
- ♦ Add 50 ml of nitric acid boil until all bromine is expelled. Cool and add 50 ml water.
- ♦ Filter through Whatman No.5 filter paper or equivalent into 250 ml volumetric flask. Wash beaker and paper thoroughly with hot water and make up the volume.
- ♦ Take an aliquot containing 50-100 mg of S in 400 ml beaker and evaporate to 1 or 2 ml on hot plate.
- ♦ Add 10 ml. HCl and 50 ml of water and heat to boiling.

- ◆ Add slowly 15 ml of 10% barium chloride solution with constant stirring and digest at low temperature hot plate or on steam bath for 1 hour. Remove from hot plate and allow the precipitate to settle for 4 hours.
- ◆ Filter through Gooch Crucible previously heated and weighed. Wash 8-10 times with hot water till the filtrate is free from chlorides (test 1% silver nitrate solution).
- ◆ Dry and ignite the precipitate at 800° C to a constant weight. cool in desiccator over magnesium perchlorate and weigh.

Calculation

$$\% S = \frac{\text{BaSO}_4 \text{ precipitate} \times 0.1374 \times 100}{\text{gm of sample in aliquot}}$$

Example :

If 2 gm of magnesium sulphate fertilizer is dissolved in 250 ml, out of which 25 ml aliquot has been taken for precipitation and the weight of the precipitate is 0.150 gm, then.

$$S (\%) = \frac{0.1500 \times 0.1374 \times 100}{2} \times \frac{250}{25} = 10.30\%$$

$$SO_4 (\%) = 10.30 \times 4 = 41.20\%$$

Note : In case the sample contains only sulphate sulphur, the step 2 and 3 can be eliminated.

Reference book :

H.L.S. Tandon (1995) Methods of Analysis of soil, water, plant and fertilizers, ..FDCC, New Delhi. pp. 138-139.

EXERCISE NO.8

DETERMINATION OF ZINC CONTENT FROM MICRONUTRIENT FERTILIZER [EDTA METHOD]

Principle :

Ethylenediamine tetra acetic acid (EDTA) forms complexes with divalent cations, like Ca^{+2} , Mg^{+2} , Zn^{+2} . The metal replaces hydrogen atoms of (-COOH) groups and is also linked by coordinate bonds to nitrogen atoms of EDTA. This principle is used in determination of cations such as Ca^{+2} , Mg^{+2} , Zn^{+2} , Cu^{+2} etc. by titration. The indicator eriochrome Black T is used to detect the end point.

Reagents :

- 1) EDTA (0.01 N) : Dissolve accurately weighed 2.00 gm sodium salt of EDTA in 100 ml distilled water and finally dilute to 1 litre in volumetric flask.
- 2) Standard zinc solution : weigh 1.250 gm of zinc metal and dissolve in 20 ml 1:1 warm HCl. Dilute and make final volume 500 ml.
- 3) Ammonium hydroxide - 20 %.
- 4) Ammonium chloride
- 5) Sodium cyanide
- 6) Formaldehyde solution : Dilute 1 volume of formaldehyde 36 % (M/V) with 80 volumes of water.
- 7) Eriochrome black - T mix 1 gm of EBT with 100 gm of NaCl

Procedure :

- 1) Standardization of EDTA : Pipette 50 ml of standard solution zinc and transfer in a clean beaker. Add NH_4OH until permanent precipitate is formed, add 10 ml in excess. Dilute with about 400 ml of distilled water. Add few specks of indicator. Titrate the red solution with EDTA to a clear blue colour end point.
- 2) Determination : Dissolve 0.5 gm of material in about 25 ml water and add 0.1 gm NH_4Cl and 0.5 gm NaCN (Add more NaCN, if precipitate formed, does not dissolve completely). Add approximately 75 ml water and 10-20 ml NH_4OH . Add few specks of indicator. Mix and add 20 ml formaldehyde solution. Immediately titrate with EDTA till clear blue colour end point.

$$\text{Percent zinc in sample} = 12.5 \times \frac{V_1}{V_2 \times M}$$

Where,

V_1 = Vol. of EDTA used with sample in determination.

V_2 = vol. of EDTA used in standardization.

M = Mass of sample taken

Reference :

1. A.K. Gupta (2007). Practical Manual of Agril. Chemistry. pp. 105-106.

EXERCISE NO.9

STUDY OF PLANT PROTECTION APPLIANCES

EXERCISE NO.10

CALCULATION OF DOSES OF INSECTICIDES

I. Preparation of Spray Solution

1 Calibrations of Spray formulations:

Application of pesticides in proper concentration is necessary for desired control of the pest particularly when the pesticides are supplied as spray in high volumes by conventional sprayer. Lower concentrations than those prescribed for spraying result in poor or no control of the pest while those with higher concentrations result in wastage of pesticides or may even produce phytotoxic effect on crops.

In view of the availability of various formulations such as suspensions (w.p.) emulsions (E.C.) solutions containing different proportions of active ingredients (actual, toxicant) they are necessarily to be diluted with water to obtain desired concentrations before they are applied to the crops.

The percentage of technical ingredient is generally indicated on the containers of these formulated insecticides. The diluted sprays are prepared on the basis of these percentages by calculating the quantity of water and formulated insecticides to get the proper concentration required for spraying. The following formula would help in working out a quantity of insecticide required to give a known concentration or concentration of toxicant in spray.

Percentage of the toxicant in trade product available in the market	x	Quantity of formulated insecticide to be mixed	=	Percentage of actual toxicant in the spray material	x	Quantity of spray material required.
--	---	---	---	--	---	--

The following few examples will illustrate the calibration and estimation of spray formulations required for spraying the crops with high volume spray. The efficiency of the pesticidal application will depend upon how much toxicant is deposited per unit area and to what extent, the plant surface is covered with the pesticide. The best application would, therefore, be the one, in which there is full coverage. In case of high volume or conventional sprays, the factors like the concentration of finished spray and its quantity per ha is important in carrying out the spray operation.



1. Quantity of insecticide required :

The requirement of quantity of commercial formulation of the insecticide can be calculated by the formula.

$$= \frac{\text{Volume of spray fluid} \times \text{Strength of the spray solution desired (\%)}}{\text{Strength of commercial formulation (\%)}}$$

2. Strength of the finished spray solution:

To calculate the strength of a finished spray solution when a known quantity of chemical is added to known quantity of water, the following formulate may be adopted.

$$= \frac{\text{Quantity of the insecticide used} \times \text{Strength of the insecticide (\%)}}{\text{Quantity of finished spray solution required}}$$

3. In case of granules

$$\text{Quantity of chemical needed} = \frac{\text{Recommended dose a.i./ha} \times 100}{\text{Area} \times \% \text{ a.i. of insecticide}}$$

Points to be considered in spray fluid preparation / spraying

- Use good quality water to prepare spray fluid.
- Prepare spray fluid in clean drum or plastic buckets.
- For missing pesticide, use long handled stir.
- Always prepare spray fluid just before use.
- Spraying should be done under ideal weather conditions.
- The walking speed of the operator should be uniform to ensure even coverage of spray chemicals in the target area.

Botanicals

Among the plant derivatives, neem oil 0.5 to 3 per cent and neem seed kernel extract 5 per cent with teepol 0.05 per cent are quite effective against major pests of rice, pulses, sucking pests of cotton, vegetables etc.

Neem oil (NO): To get a 3 per cent solution first mix 30 ml of neem oil with 5 ml of sticking agent teepol until white emulsion is formed. Then add one litre of water and mix thoroughly for use of spray fluid.

Neem seed kernel extract (NSKE): Further preparation of 5 per cent NSKE, take 50 gm of powdered seed kernel and soak it in small quantity of water, over night. Filter through muslin cloth and make up the volume to one litre. Add one ml of teepol per litre before spraying high volume sprayer.

Calibration of Spray Formulations

Example No.1

A farmer wants to spray his 4 hectares of cotton crop with 0.012% fenvalerate 20 E.C. at the rate of 500 litres of spray material per ha. Calculate how much quantity of fenvalerate 20 E.C. will be required for spraying ?

Answer:-

$$20 \times Y = 0.012 \times 500$$

$$Y = \frac{0.012 \times 500}{20} = 0.3 \text{ lits / ha}$$

For 4 ha = $0.3 \times 4 = 1.2$ lits of fenvalerate 20 E.C. will be required.

Example No.2

2.00 kg of carbaryl 50 W.P. is applied for the control of onion thrips at the rate of 500 lits of spray material per hectare. Calculate the concentration at which the carbaryl is sprayed on onion.

Answer:-

$$50 \times 2 = Y \times 500$$

$$Y = \frac{50 \times 2}{500} = 0.2\% \text{ concentration.}$$

Example No.3

How much area will be covered with the 2 litres of dimethoate 30 EC if it is applied at the rate 0.03% concentration in 500 litres of spray material per hectare ?

Answer:-

1. Calculate first the required quantity of Dimethoate per ha by using formula

$$\text{i.e. } 30 \times Y = 0.03 \times 500$$

$$Y = \frac{0.03 \times 500}{30}$$

$$Y = 0.9 \text{ lits of Dimethoate / ha.}$$

2. On this basis calculate how much area will be covered by 2.0 lits.

$$= 0.5 \text{ lits is required for 1 ha so for 2 lits} = 2/0.5 = 4 \text{ ha.}$$

Answer = 4.00 ha of area will be covered by 2 lits of Dimethoate 30 EC at 0.03 % concentration.

Example No. 4

Cultivator has got 4.00 hectares of mango, orchard planted at a distance of 10 x 10 mts. He has been advised to apply one spray each with monocrotophos 36 W.S.C. and quinalphos 25 EC at 0.04 & 0.05% concentration respectively at an interval of 15 days, using 10 lits of water per tree at each spraying. Calculate the total quantity of insecticidal formulations required and the quantity of formulation required per tree.

Answer:-

Steps _

Given

1. Area = 4 ha
2. Spacing = 10 x 10 mt
3. No of sprayings = 2 i.e. one with each insecticide
4. Concentration of spraying solutions.

a) Monocrotophos 36 WSC = 0.04%

b) Quinalphos 25 EC = 0.05%.

5. Quantity of water used per tree = 10 lits.

Required (to be calculated)

1. No. of trees / orchards in 4 ha ?
2. Total Qty of insecticidal formulation required? 3 Qty of insecticidal formulations reqd / tree ?

Calculations:

1 ha = 10,000/- sq. mt.

Spacing = 10 x 10 = 100 sq. mt.

No. of plants in 1 ha = $\frac{10,000}{100} = 100$ Nos

No. of plants in 4 ha = 4 x 100 = 400 Nos.

Formula:

Quantity of insecticidal formulation required x strength / concentration (Qty of A.I.) of a commercial / trade formulation = Quantity of water / spray solution x concentration of a final spray solution.

For Monocrotophos 30 WSC, 1 tree requires 10 lits of water.

By putting in formula

$$y \times 36 = 0.04 \times 10$$

$$Y = \frac{0.04 \times 10}{36} = 0.0111 \text{ Nos}$$

i.e. 11 ml. of monocrotophos 36 E.C. will be reqd /tree. 1 tree requires 11 ml, so 400 trees will require

$$11 \times 400 = 4400 \text{ ml, i.e. 4.4 lits.}$$

For Quinalphos 25 EC, 1 tree requires 10 lits of water.

By putting figs in formula

$$y \times 25 = 0.05 \times 10$$

$$Y = \frac{0.05 \times 10}{25} = 0.02 \text{ lits i.e. 20 ml.}$$

i.e. 20 ml. of quinalphos 25 EC will be reqd /tree.

On this basis calculate how much qty will be reqd for 4 ha. So for 400 nos of trees =

$$400 \times 20 = 8000 \text{ ml, i.e. 8.0 lits.}$$

Total quantity of Monocrotophos 36 WSC reqd. for 4 ha. = 4.4 lits.

Per tree quantity of Monocrotophos 36 WSC reqd. = 11 ml.

Total quantity of quinalphos 25 EC reqd for 4 ha = 8.0 lits.

Quantity of quinalphos 25 EC reqd /tree = 20 ml.

If a quantity of A. I. (Active ingredient) is given

Example No. 5

0.450 lits of AI of Dimethoate 30 EC is applied on 3 ha cropped area of cotton using 500 lits of water per hectare. Calculate the concentration of spray solution and the quantity of insecticidal formulation required/ha.

Answer:-

A I means the quantity of actual present in the formulation. Dimethoate 30 EC means, 300 ml. of active ingredient (actual qty. of toxicant) is present in 1000 ml. of the formulation.
Given

1. Insecticidal formulation used = Dimethoate 30 EC
2. Qty. of AI. applied = 0.4750 lits.
3. Area covered = 3.00 ha.
4. Qty of water used /ha = 500 lits.

To be calculated

1. Qty of insecticidal formulation which will contain 0.450 lits of AI = y
2. Concentration of a spray solution = y

First calculate the quantity of insecticidal formulation that will give 0.450 lits a.i. by using a

formula

$$\text{Quantity of commercial formulation required / used} = \frac{\text{Quantity of actual ingredient (a.i.) required / used}}{\text{Percentage toxicant in commercial formulation}} \times 100$$

$$Y = \frac{0.450}{30} \times 100 = 1.5 \text{ lits}$$

1.5 lits of Dimethoate 30 EC formulation will required for 3 ha

Likewise percentage concentration of toxicant used in spray solution

$$= \frac{\text{a.i.}}{\text{Quantity of spray solution used}} \times 100$$

Now to calculate the concentration of a spray solution.

First calculate the quantity required for 1 ha.

$$\text{i.e.} \quad \frac{1.5}{3} = 0.5 \text{ lits / ha}$$

Now put the figures in the formula

Qty of insecticidal formulation reqd.	x	strength of a give	=	conc. of a spray solution x	Qty of water
0.5	x	30	=	y	500

$$\frac{0.5 \times 30}{500} = y$$

So $y = 0.03\%$ concentration.

Answer =

1. Concentration of spray solution = 0.03%.

2. Qty dimethoate 30 EE = 0.5 lits / ha.

Example No.5

5% chlordane dust is used for the control of termites @ 65 kg/ha calculate the rate at which actual toxicant of chlordane is used per ha for the control of termites

Answers:-

Given

1. Insecticide used = Chlordane 5 D

2. Qty of insecticidal formulation used = 65 kg

To be calculated

1. Rate at which A.I. used ha = y

$$\text{Quantity of a.i. required used 1 per ha} = \frac{\text{Quantity of commercial formulation used} \times \text{Percentage toxicant in commercial formulation}}{100}$$

$$= \frac{65 \times 5}{100}$$

$$y = 3.25 \text{ Kg}$$

Answers = 3.25 kg A.I of chlordane 5 D is used / ha

Example No.6

Prepare 100 kg of 0.75 per cent rotenone dust from 5% rotenone dust powder by using a pyrophyllite as a diluting agent.

Answers:-

5 kg a.i. is available in 100 kg of 5 % dust formulation

So, for 0.75 kg a.i. = 15 kg 5% dust formulation will be required

So, 100 kg of 0.75% rotenone will be prepared by adding = $100 - 15 = 85$ kg of pyrophyllite to dilute 15 kg of rotenone dust.

HOME WORK

Ex. No. 1:- How much quantity of quinalphos 25 EC will be required, if 0.05% spray is to be applied @ 1 000 litres / ha.

Ex. No. 2:- 0.035 % spray of Endosulfan 35 EC was applied using 500 lits. of water. How much quantity of Endosulfan 35 EC will be required for one ha.

Ex. No. 3:- What will be the concentration of the final spray material if 1.00 lits. of Monocrotophos 36 WSC is added in 500 ^{lit} of water.

Ex. No. 4:- Phorate 10 G have been applied @ 20 kg /ha. to mango orchard planted at distance of 10 x10 m². Work out the a.i. of phoratel / tree.

EXERCISE NO.11

Pesticide Formulations

STUDY OF FORMULATION OF PESTICIDES

Pesticides are not usually applied in pure form (active ingredient), since they are highly toxic and quantity available for application is low and hence they are diluted with inert materials like talc or with water combining with other materials such as solvents, wetting agents, stickers etc. The final product is the formulated pesticide and it is ready for use.

The process involved in converting concentrated forms of active ingredient into a relatively diluted form is known as formulation. In other words, active ingredient mixed with a carrier is known as formulation.

Types of pesticidal formulations:

According to the mode of application, the types of formulation are as follows:

A. Dry Formulations:

1. Dusts or powder for dusting
2. Wettable powder
3. Seed dresser
4. Granules
5. Solid fumigants
 - Powder
 - Tablets
 - Balls
6. Capsules
7. Dry poison baits
8. Soaps
9. Insecticides fertilizer mixtures
10. Solid poison baits.

B. Wet or Liquid Formulations:

1. Emulsifiable concentrates
2. Solutions
3. Concentrated insecticide liquids
4. Aerosoles
5. Paste
6. Liquid poison baits

Besides these formulations, insecticides are also used as vapours gases, or smokes or fogs etc. These are usually used in pure form unless they are inflammable.

Most commonly used formulations are:

1. Emulsifiable concentrates
2. Wettable powder
3. Dusts
4. Granules

1) Emulsifiable concentrates:

The formulation contains the toxicant, a solvent for the toxicant and an emulsifying agent. It is a clear solution and yields an emulsion of oil in water, when diluted with water to spray strength. When sprayed the solvent evaporates quickly leaving a deposit of toxicant from which water also

evaporates. Emulsifying agents used are alkaline soaps, organic amines, carbohydrates, gum, lipids, proteins, sulphates of long chain alcohols.

The addition of emulsifying agents have the following specific purposes:

- a. Dilution of a water insoluble chemical with water is made possible.
- b. The surface tension of the spray is reduced allowing it to spread and wet the treated surface.
- c. Better contact with insect cuticle is made possible.
- d. Droplet size of the emulsion is greatly influenced by the kind and amount of emulsifier used.

The solvents generally used are petroleum hydrocarbons, other solvents used are Isopropyl alcohol, methyl, naphthalenes and xylene.

Examples:- Endosulfan 35 EC, Dimethoate 30 EC, etc.

2. Water dispersible powders (WSP) or Wettable powders (WP):

Wettable powder is a powdered formulation which yields a rather stable suspension when diluted with water. The active ingredient in such formulations ranges from 15 to 90%. It is formulated by blending the toxicant with a diluent such as attapulgit, a surface active agent and an auxiliary material such as sodium salts. Sometimes stickers are added to improve retention on plants and other surfaces. Though the particles of a suspension adhere well to treated surfaces, they do not penetrate and thus are easily washed off. However suspensions are more effective than dusts.

Example: Carbaryl 50 WP or WDP.

3. Dusts:

In a dust formulation the toxicant is diluted either by mixing with or by impregnation on a suitable finely divided "Carrier". The carrier may be an organic flour (walnut shell flour, wood bark) or pulverised mineral (Sulphur, lime, gypsum, talc) or clay (attapulgit, bentonite, kaolins). The toxicant in a dust formulation ranges from 0.65% to 25%. Dusts are defined as those formulations having particle size less than 100 microns. With decrease in particle size the toxicity of the formulation increases. The dusts should flow freely and must not 'cake' or 'Ball' in the hopper. Dust application must be done in a calm weather and early in the morning when the plants are wet with dew.

Example: Carbaryl 10% , chlordane 10% dust, Endosulfan 4% dust, Lindane 0.65% and 1.3 % dust.

Advantages:

1. Dusts can be used where water supply is difficult and inadequate i. e. areas of water scarcity.
2. Quantity required per hectare is less.

-
3. Appliances used for dusting are simple and hence dust application is easier.
 4. Application of dust formulation is faster than spray application.
 5. Dusts and dusters are light in weight and hence can be used in hilly areas or muddy fields.
 6. Dust is cheaper formulation and require less cost.

Disadvantages:

1. Drift problems-dusts are likely to blow away due to wind velocity.
2. It increases the cost of carrier as compared to water in spray.
3. Due to less deposition on, plants efficiency is decreased.

4. Granules:

In a granular formulation the particle is composed of a base, such as an inert material or vegetable carrier impregnated or fused with the toxicant which is released from the formulation in its intact form. The particle size ranges from 0.25 mm to 2.38 mm diameter but usually 250 to 1250 microns. The formulation contains 2 to 10% concentration of the toxicant. The formulations are used in the control of weeds, plants diseases, and insect pests, nematodes, snails, rodents etc.

Examples:- Phorate 10G, Carbofuran 3G, Quinalphos 5G, Sevidol 4:4, Disulfoton 5G, etc.

Advantages:

1. There is a very little drift.
2. No undue loss of insecticide.
3. Undesirable contamination is prevented.
4. Residue problem is less as granules do not adhere to plant surface.
5. Release of toxic material is achieved over a long period than does a spray deposit.
6. Water is not required for application.
7. Less harmful to natural enemies of the pest species.

Disadvantages:

1. Not as effective as spray against most crawling insects.
2. Scorching may occur if the toxicant is concentrated in smaller volume of carrier.

4. Flowable (F) :

Flowable is a pesticide formulation in which the active ingredient is wet milled with a clay diluent and water. Flowables must be constantly agitated to prevent the insecticide from coming out of suspension and settling.

5. Ultra low volume concentrates (ULV) :

□

They are special kind of high concentrate salutations and are applied without special aerial or ground equipment to produce extremely fine spray.

For application as gas or vapour

1. Fumigants :

Fumigants are pesticides in the form of poisonous gases that kill when absorbed or inhaled. Most of the fumigants are liquid and are mixtures of two or more gases.

2. Smoke generators :

They are used in the form of coil like strips containing pyrethrum, oxidant and wood dust for the control of mosquitoes. When ignited, these coils release vapours.

3. Aerosols :

Aerosol contains a small amount of pesticide that is driven through a fine opening by a chemically inactive gas under pressure when the nozzle is triggered (or) by burning toxicant or vapourizing it with that. The toxicant is suspended as minute particles (0.1 - 50 w/w) in air as a fog or mist. It consists of toxicant (2%), solvent (10%), knockdown agent (2%) and propellant (86%).

Other formulations

1. Poison bait :

These mixtures of an insecticide with food attractive to the target pests.

2. Seed dressers :

This consists of an active ingredient in carrier material with an adhesive for better coating of the chemical on the seeds.

3. Tablets :

It consists of toxicant, a carrier to prevent the flammability.

4. Insecticide paints and polishes :

Toxicant is produced in the form of paint/polish and can be applied as such by using a brush.

5. Encapsulated fumigants :

The fumigant is impregnated in some inert material and sealed in plastic containers. Cut open the plastic container before use.

Adjuvants:

These are supplementary agents do not contribute directly to the toxic action of pesticides

□

but are meant for improving physical conditions of pesticides so that pesticides become more effective in action. These adjuvants include dust carriers, stabilizer, solvents, emulsifier, wetting agents, spreading agents, dispersing agents, stickers, softeners, deodorants etc.

1. Emulsifiers:

In order to obtain the stable mixture of organic solvents (used to dissolve the toxicant) and water, surface active substances, known as emulsifiers or emulsifying agents are incorporated to the emulsifiable concentrates. The emulsifier form an interphase between the water and oil droplets, and give stability to the emulsion.

Example:- Alkaline soaps, carbohydrates, gum, lipids, proteins, sulphates of long chain alcohol organic amines, saponins etc.

2. Wetting and spreading agents (Dispersing agents):

These are generally used in the preparation of wettable powders. Since most of the plants and insect cuticle are provided with lipid layers, which are strongly hydrophobic, and water sprays tend to form droplets due to surface tension. In order to lower the surface tension of the spray material thereby making it wet and spread well on the treated surfaces, wetting and spreading agents are incorporated in the formulation.

Examples:- Soaps, besides being emulsifier also act as wetting and spreading agents. Teepol, Lorol, Sulphonated petroleum like Gardinol, Alkyl sulphates or sulphonated alcohol, Tergitols, marsolates, Triton x-100 etc.

3. Stickers or adhesives:

These are added to spray formulation to help the spray deposits to adhere well to the treated surfaces and to increase the retention power to the spray deposits.

Examples:- Casein, soya bean flour, bentonites, dried skimmed milk, gum arabic, clays, petroleum and vegetable oils, gelatine etc.

EXERCISE NO.12

STUDY OF PESTICIDE APPLICATION TECHNIQUES

EXERCISE NO.13

HERBICIDE LABEL INFORMATION AND COMPUTATION OF HERBICIDE DOSES

Significance of symbols on the Label :- Several signal words or symbols based on the toxicity of the product are required by law to group them into respective categories of toxicity. There are 4 categories of toxicity and each of which is indicated by an appropriate symbol and signal as follows :

Toxicity category	Acute oral toxicity LD 50 mg/kg	Colour of triangle	Signal word required on label	Warning symbol on the label
1. Extremely toxic	0-50	Bright Red	Word 'POISON' Printed in red	Skull and cross bones
2. Highly toxic	51-500	Bright yellow	Word 'POISON' Printed red	--
3. Moderately toxic	501-5000	Bright blue	Word 'Danger'	--
4. slightly toxic	5000	Bright green	Word 'Caution'	--

Precautions :

- 1) Read all the information given on the labels of the containers.
- 2) Note the symbols written on the labels very carefully.

Materials required :

- i) Empty herbicide containers bearing labels.
- ii) Sample labels of various types of commercial herbicides.

Procedure :

Examine a few commercial herbicide containers and make a list of all types of information given on the labels.

Observations :

The student should note down the information available on the labels against each item in the following table.

Sr. No.	Item	Herbicide			
		1	2	3	4
1	Chemical name				
2	Common name				
3	Trade name				
4	Manufacturers address				
5	Percentage of active ingredients				
6	Percentage of carrier, filler and adjuvant				
7	Different between different products containing the same active sub-gradient				
8	Net content, if given				
9	Treatment for accidental exposure or poisoning				
10	Date of manufacturer				
11	Date of expiry				
12	Misuse statement, if any				
13	Direction for use, if any				
14	Storage and disposal of the product, if any				
15	Warranty statement, if any				
16	Precautionary statement if any				
17	Name of the crops for which the herbicide is recommended				
18	Any other information				

Date:

COMPUTATION OF HERBICIDE DOSES

- ✓ **Object :-**
- i) To know weight of commercial product required per hectare.
 - ii) To know quantity of formulated herbicide required per unit area
 - iii) To know quantity of formulated herbicide required per liter water

Rate of application is the amount of active ingredient or acid equivalent of a herbicide applied per unit area. It is usually given in terms of kg ai or a.e. ha⁻¹

$$1) \text{ Quantity of herbicide required kg/ha} = \frac{\text{Rate of application of kg ai / ha}}{\text{Percentage content of a.i. in the product}} \times 100$$

✓ **Example :-** Find out the quantity of atrataf wettable powder to be sprayed in sugarcane of an area of one ha. If (1) the rate of application is 2 kg ai/ha, and percentage of a.i. in the product is 50. Thus the quantity of atrataf required /ha

$$= \frac{2.5 \times 100}{50} = 5 \text{ kg/ha}$$

Answer :- Atrataf required for one ha sugarcane = 5 kg.

✓ **Example 2:**

Which one of the herbicide formulation is cheaper to apply in 10 ha. of wheat crop (a) 2, 4-d ester with 400 gm ai / litre and (b) 2, 4-D amine salt with 500 gm ai./ litre. The recommended doses of application are 0.25 kg ester ha and 0.5 kg amine ha. The cost of commercial material of ester is Rs. 50 /litre and amine Rs. 35 /litre.

Solution :

✓ a) Total active ingredient for ester needed for 10 ha.

$$= 10 \times 0.25 = 2.5 \text{ kg ester.}$$

40 kg present in 100 lits.

$$\therefore 2.5 \text{ kg} \text{ ----- } Y \quad Y = \frac{100 \times 2.5}{40} = 6.25 \text{ L.}$$

= 6.25 L Commercial ester

$$= \text{Cost of 6.25 Ester} = 6.25 \times 50 = \text{Rs } 312.50$$

b) Total active ingredient for amine needed for 10 ha.

$$= 10 \times 0.50 = 5.0 \text{ kg Amine}$$

50 kg a.i. is present in 100 kg of commercial product

$$\therefore 5 \text{ kg} \xrightarrow{\quad\quad\quad} Y \text{ kg}$$

$$= \frac{100 \times 5}{50} = 10 \text{ kg}$$

Cost of 10 kg amine = $10 \times 35 = \text{Rs } 350$

Answer : Ester formulation is cheaper than the amine formulation.

Example 3 : Find out quantity of Alachlor needed to spray in 10 ha area

- 1) Recommended dose = 0.5 kg ai/ha
- 2) P.C. of ai commercial material is 50 %

Solution :

$$\text{Volume of alachlor needed / ha} = \frac{\text{Rate of application kg a.i. /ha}}{\% \text{ content of a.i. in commercial material}} \times 100$$

$$\text{The quantity of alachlor needed for 1 ha.} = \frac{0.5}{50} \times 100 = 1 \text{ litre / ha}$$

$$\text{The quantity of alachlor needed for 10 ha} = 10 \times 1 = 10 \text{ L}$$

Assignment: Find out quantity of simazine wettable powder to be sprayed in one hectare area if

- 1) Rate of application = 3 kg ai/ha
- 2) Active ingredient = 50 %

II) Quantity of formulated herbicide required per unit area

Table Quantities of formulated herbicide required per unit area at different rates and active ingredients.

Active ingredient (%)	Rate (kg a.i ha ⁻¹)	Quantity (g or ml) of formulated product per m ² area			
		1 m	10 m	100 m	1000 m
20	0.5	0.25	2.5	25.0	250.0
	1.0	0.50	5.0	50.0	500.0
25	0.5	0.20	2.0	20.0	200.0
	1.0	0.40	4.0	40.0	400.0
35	0.5	0.143	1.43	14.30	143.0
	1.0	0.286	2.86	28.60	286.0
40	0.5	0.125	1.25	12.50	125.0
	1.0	0.250	2.50	25.00	250.0
50	0.5	0.10	1.00	10.00	100.0
	1.0	0.20	2.00	20.00	200.0

$$\text{Quantities of formulated herbicide} = \frac{\text{Rate of application of ai/ha} \times \text{unit area (m}^2\text{)} \times 100}{\text{Percentage content of a.i. in the product} \times 10000 \text{ (m}^2\text{)}} \\ \text{Per unit area}$$

Assignment: Suppose percentage content of ai in the herbicide is 35 and the rate of application of ai 1 kg (1000 g) / ha. Calculate quantity of formulated herbicide for 1000 (m²) area.

III) Quantities of formulated herbicide per litre water

Quantities of formulated herbicide required per litre water at different rates of a.i. assuming spray volume of 500 l ha⁻¹ is given in table.

TABLE : Quantities of formulated herbicide per litre of water

Active ingredient (%)	Rate (kg a.i ha ⁻¹)	Quantity (g or ml) of formulated product litre of water
20	0.5	5.0
	1.0	10.0
25	0.5	4.0
	1.0	8.0
35	0.5	2.86
	1.0	5.72
40	0.5	2.50
	1.0	5.00
50	0.5	2.00
	1.0	4.00

$$\text{Quantities of formulated herbicide} = \frac{\text{Rate of application of kg a.i. / ha}}{\text{Percentage content of a.i. in the product} \times \text{volume of water used per ha.}} \\ \text{Per litre water}$$

Example :- Work out quantity of Alachlor 50 % EC per litre water

- 1) Rate of application of ai - 1 kg/ha
- 2) Volume of water used - 500 litre/ha

PARTS PER MILLION (PPM) :-

It refers to the no. of parts by weight or volume of a constituent in 1,000,000 parts of final mixture, by weight or volume. The stated concentration should tell whether, PPM is measured by weight or volume for herbicidal purposes. It usually refers to a given weight of a chemical in a given volume of spray.

$$\text{Percent} = \frac{\text{PPM}}{10,000}, \text{ PPM} = \text{percent} \times 10,000$$

Example :- 1) Express the concentration of solution in ppm if 3.5 kg of simazine is mixed with 500 litre water.

2) Find out the quantity of 2,4 D amine, 50% WP and water needed for spraying 5 ha of wheat crop with a solution of 6000 ppm. The recommended dose is 0.25 kg ai/ha.

EXERCISE NO.14

EQUIPMENTS USED FOR HERBICIDE APPLICATION AND CALIBRATION.

DEMONSTRATION OF METHODS OF HERBICIDE APPLICATION

Object : To know various equipments required for herbicide application and its calibration.

HERBICIDE APPLIANCES

Generally herbicides are applied in the form of solution or granules. Spraying is the most common method of application of herbicides formulated as wettable powders, emulsifiable concentrates and solution concentrates. When herbicides are formulated as granules, they are applied by hand or with the help of granular applicator.

a) Herbicides spraying :

Herbicides are mixed with suitable carrier to facilitate uniform distribution and even coverage over the area to be treated. Herbicides sprayers are of two types : hand operated sprayers and power driven sprayers. Depending on the volume of discharge of the spray fluid per unit time are classified as high volume and low volume sprayers.

b) Hand operated sprayers

1. Knapsack sprayers:

The hydraulic knapsack sprayer with a capacity of 10 to 15 litres is the most useful and widely used sprayer in India for herbicide application.

2. Pneumatic or compressed sprayer:

These pumps force air into an airtight tank containing the spray liquid. The air pressure moves the spray liquid into the nozzle where it gets atomized before leaving the sprayers as fine spray.

3. Foot sprayers (=Pedal Pump Sprayers)

The foot sprayer is very popular in many developing countries for the application of herbicides on comparatively large holdings. The pump lever of a foot sprayer has a pedal. The lever is conveniently worked with foot. The sprayer has provision for 1-2 long delivery hoses, each fitted with either a lance or a 3-6 nozzles boom. A pedal pump sprayer uses an external spray tank through an intake pipe fitted with a sieve at its sucking end. It develops a spray pressure of 17-21 kg cm⁻² and its output with one lance is about 1 ha per day of 8 hours.

c) Tractor powered sprayers

Tractor mounted sprayers work under a spray pressure of 1.4-2.8 kg cm⁻². These are fitted with multi nozzle booms which make them very useful herbicide application equipments for the large holding farmers. Other advantages of tractor-run sprayers include high uniformity of the spray and utilization of the tractor during idle time.

MAJOR COMPONENTS OF SPRAYERS

The important components of a sprayer are (i) pump (ii) power source (iii) tank (iv) pressure gauge and (v) pressure regulator.

(i) Pump

Any spray liquid must be atomized before it leaves the spray nozzle. A pump provides the necessary pressure for this purpose.

(ii) source of power

source of power is needed to run the sprayer pumps. This source of power may be (a) manual (b) traction (c) motor or (d) tractor and aircraft engines.

(iii) Spray tank

A sprayer have either a built in tank or separate tank to carry the spray liquid. The tank should be large enough to avoid frequent refilling but at the same time, not unwieldy to carry. Depending upon the kind of sprayer, the tank size varies from 10-15 to 2250 litres and sometimes even more. A tank is provided with a large opening, fitted with strainer and cap to fill the spray liquid. Small tank opening can make filling and cleaning of the tank difficult.

(iv) Agitator

Most spray tanks carry an agitator. It may be either a mechanical or hydraulic type. The agitator keeps the spray liquid components in homogeneous mixture.

(v) Pressure gauge and pressure regulator :

is generally provided to power sprayer. Tractor mounted sprayers work under a spray pressure of 1.4 to 2.8 kg cm⁻². Optimum pressure in case of knapsack sprayer to be maintained 0.7 kg cm⁻² to 3.00 kg cm⁻².

Sprayer calibration

Accurate calibration of a sprayer is essential if herbicides are to be used safely and effectively. A sublethal dose of spray will fail to give satisfactory control of weeds. An overdose will increase costs besides affecting the crop or resulting in accumulation of toxic residues in the soil.

The objective of calibrating any sprayer utilizing a liquid (water) as a carrier is to uniformly distribute herbicide over a given area and to determine and adjust the volume of carrier so that the sprayer will discharge to a known area under a given set of condition. Proper sprayer calibration is essential for the application of the correct amount of herbicides.

Achievement of a desired application rate is governed by :

1. Type of nozzle used
2. size of the nozzle orifice
3. spray pressure used
4. spraying speed
5. viscosity of the spray liquid

1. Nozzles

Nozzles break the pressurized spray. Solution into droplets for application to the target. The function of the nozzle is to accelerate and disintegrate the flow of spray liquid passing through it into droplets to form a spray.

In herbicide use, eight kinds of nozzles are common. these are as :

- | | |
|--------------------|------------------------|
| 1) Flat fan | 2) Solid cone |
| 3) Hollow cone | 4) Flood jet deflector |
| 5) Triple action | 6) Low volume |
| 7) Centrifugal and | 8) Blast nozzles. |

(a) cone type : In the cone type nozzle, the liquid is force through one or more tangential or helical passages in to a swirl chamber through which the liquid passes to a circular orifice at a high rotational velocity emerges from an air core within the orifice and swirl chamber. The liquid emerges from the orifice as a hollow cone.

In the case of a solid cone nozzle, the liquid also passes centrally through the nozzle to fill the air space. Cone nozzles are widely used for insecticide and fungicide application as also for spot application of post-emergence herbicides.

(b) Fan and deflector type :

Herbicide spraying is mostly done with fan and flooding or deflector type nozzles as they produce a more even distribution of spray and uniform coverage than the cone spray types.

In the case of fan nozzle the tip has a lenticular or rectangular orifice behind which two streams of liquid meet because of the shape of the bore. Fan nozzles are ideal for spraying herbicides on flat surfaces and for band spraying in row crops.

In the deflector nozzle also known as flooding, anvil or impact nozzle, a jet of liquid passes through a relatively large orifice and strikes a smooth surface at a high angle of incidence to form a fan shaped spray pattern.

2. Size of the nozzle orifice

The nozzle orifice should be optimum so that the spray neither delivers coarse droplets nor the droplets escape in the form a mist or fog, crating a drift hazard. Selection of optimum nozzle orifice (WFN 62) delivers a good spray without any drift.

Table : Floodjet Nozzle Rating at different pressures

Nozzle code No. WFN	5 p.s.i. Discharge spray per Min. Angle		10 p.s.i. Discharge spray per Min. Angle		15 p.s.i. Discharge spray per Min. Angle	
	in ml.	in°	in ml.	in°	in ml.	in°
24	-	-	172	25	220	40
40	350	30	470	40	550	50
62	900	80	1230	95	1500	105
78	1480	100	2040	110	2480	115

3. Spray pressure used :

When the delivery pressure is low, the liquid escapes from the nozzle tip as liquid film, which, when expands forms droplets at the outer edge. At high pressure, the droplets escape in the form of a mist or fog creating a drift hazard. For proper spraying using deflector nozzles, the hand operated knapsack sprayer should maintained a pressure of 10 to 15 pounds per square inch (0.7 to 1.05 kg/cm²)

4. Walking speed :-

Increasing walking speed decreases the discharge of spray and some times it causes an uneven distribution of herbicide in the soil. A steady speed of walking helps in even distribution and uniform coverage of the chemical.

5. Viscosity of the spray liquid :

The droplets from the nozzle will be smaller in size if the liquid has low surface tension and the required volume of spray solution to a given area is large. Conversely, the greater the viscosity lesser the carrier applied.

Calibration of a sprayer

The process to find out the exact quantity of carrier (water) required for spraying a given area under a set of conditions is called 'calibration'. Calibration of a sprayer is a must for spraying herbicide in the field. Calibration can be done by filling a known quantity of water into the sprayer and spraying it over a measured area.

The quantity of the water required for spraying a given area can be calculated by using the following formula.

$$Q = \frac{(V1 - V2)}{a} \times A$$

Where

Q = Quantity of water required for area to be sprayed (litres)

V1 = quantity of water taken initially

V2 = quantity of water remained after spraying

A = Area to be sprayed m²

a = measured area sprayed m²

If 100m is covered while spraying solution of 5 lit. (V1 - V2) with swath width of 1.0 m, volume required ha⁻¹ is

$$= \frac{5 \times 10000}{100 \times 1} = 500 \text{ L}$$

The area covered per hour can be calculated as shown under :

$$\text{Area (ha)/hr} = \frac{\text{Walking speed (km/hr)} \times 1000 \times \text{spray width (m)}}{M^2/\text{ha}}$$

For example, if a person is walking at 1 km/hr covering a swath of 0.6 m wide, the area covered/hr is

$$\frac{1 \times 1000 \times 0.6}{10000} = 0.06 \text{ ha/hr}$$

Area covered in one day (8 hrs) = $0.06 \times 8 = 0.48$ ha/ day

At this rate, it will take 16 hr 40 min to cover an area of one hectare. At a spray discharge rate of 30 litres/hr. it would require a spray volume of 500 litres/ha.

GRANULE APPLICATORS

Most herbicide granule applicators use gravity flow system with a rotating agitator. A Granular applicators consists of hopper in which the granules are placed, a rotating disc device to get broadcasting application pattern, a long flexible discharge tube with nozzle at the distance and a finger controlled mechanism for regulating the flow of granules. By rotating the handles, the granules are released in to tube through exit hole of the hopper. The applicators are made up of plastic and have a capacity of 1 to 10 kg.

Calibration of Granule Applicators :

Calibration of Granule applicators comprises the following steps.

- (1) Read the container label carefully to determine the application rate and particle size of the granules.
- (2) Adjust delivery openings on the applicators at approximate setting and fill the hopper with granules to be applied.
- (3) Set ground speed as it will operate in the field.
- (4) Tie some suitable container under each delivery of the applicator. Operate the unit over a measured area, simulating actual application.
- (5) Accurately weigh the granules delivered by the outlets.
- (6) Calculate the application rate of granules as –

$$\text{Kg / ha} = \frac{\text{Granules collected after the test run (in kg)} \times 10,000}{\text{Area covered in test run (in sq m)}}$$

Should the result differ from the desired, recalibrate after adjusting the orifice plates and/or the ground speed, till satisfaction.

Calculation :

- 1) Find out area sprayed by a full tank if the volume of tank is 225 litres and rate of spray / ha is 200 litres
- 2) Calculate volume of liquid required to be spray in one hectare (water)
 - i) (v1) Quantity of water taken in tank -- 15 lit.
 - ii) (v2) Quantity of water left after spraying -- 5 lit.
 - iii) (A) Area to be sprayed (m^2) -- 10000 m^2
 - iv) (a) measured area sprayed (m^2) -- 180 m^2
- 3) Find out the discharge of a sprayer from the following.
 - (i) Distance spread (length) = 200 metres
 - (ii) Width of spray swath = 1.00 metres
 - (iii) Water required to refill = 8 litres

$$\text{Discharge of sprayer} = \frac{\text{Volume of water used (in litre)} \times 10000}{\text{Width sprayed (m)} \times \text{length covered (m)}}$$

B) Draw a well labeled diagram of different types of spray pump and Nozzle.

DEMONSTRATIONS OF METHODS OF HERBICIDE APPLICATION

The methods of applications of herbicides are decided largely by their mode of action on weeds & selectivity of crops. Environment factors, convenience & cost & other important points to be considered in deciding upon a proper method of application of herbicide. The important methods of application of herbicides to cropped & non cropped lands are as follows.

a) Methods for soil application. (Pre planting or pre-emergence application)

- 1) Surface application
- 2) Sub surface or soil injection method.
- 3) Band method
- 4) Soil fumigants applications methods.

b) Methods of application of herbicide to foliage. (Post emergence application)

- 1) Broadcasting or blanket applications
- 2) directed spraying
- 3) protected spraying
- 4) spot treatment.

c) Other methods of applications :

- 1) Jar method
- 2) Wax box method
- 3) Herbicidal mulching.

(A) Methods for soil applications :-

(a) **Surface application** :- soil active herbicides are commonly applied to surface of the soil where they may be either left undisturbed or incorporated into the soil physically. When left on the soil surface the applied herbicides should be able to move into upper 2.5-4 cm of soil, under the influence of rain or irrigation, where it kills the germinating weeds. Alachlor propachlor & linuron are common surface applied herbicide in crop production. They are not physically incorporated in soil as it reduces their efficiency, probably as a result of their dilution in large volume of soil. But some soil applied herbicide EPIC (5 to 7.5 cm), Trifluralin (5cm) simazine, Atrazine Diallate and Trilalate often get it from their right incorporation into 2-3 cm. depth of soil.

- (b) **Subsurface Layering**: - Application of herbicides beneath the soil surface of soil acting herbicides by means of special equipments to provide a layer of herbicides for treating the soil at a specified depth. The most important herbicides applied by surface method are cycloate in sugarcane & Butylate in Tobacco. These herbicides are sprayed about 7.5 - 10 cm. beneath the soil surface with the help of specially designed equipments.
- (c) **Band method** :- Application of herbicide to a strip over or along crop row in continuous band. Band application of herbicides is primarily a cost saving device. Since it reduces the quantity of herbicide needed to treat a given area in the ratio of the band width to row width e.g. :- A 30cm wide band of herbicide applied over crop rows that were spaced 90 cm. apart, will require 1/3 of the quantity of herbicide needed for its application by broadcasting method. Usually 30-35 cm. band is desired to ensure control of weeds along the rows.
- (d) **Soil fumigants application method**:- This depends upon the nature of soil fumigant. It can be applied either by injection method e.g. Chloro-Picrin, under sealed plastic cover method e.g. methyl bromide & surface application methods e.g. metham.

(B) Foliage application :-

- 1) **Broadcasting / Blanket application** :- it is uniform application of herbicide to standing crop without any consideration to location of crop plants. This method of application of herbicide is also called over the top treatment. It is practiced for applying highly selective herbicide in standing crop, e.g. - 2,4-D in wheat, MCPB in Pea, 2,4-D in lucerne, Quizalofop-ethyl (Larga Super) in Soybean.
- 2) **Direct spraying** :- Herbicide is applied to particular weeds or to soil in such a manner as to ensure minimal contact with desirable plants. By this method most of the herbicide spray fall on the weeds and only a minimum quantity of herbicidal spray wet the bases and few lower leaves of crop plants. This saves the crop plants from herbicide injury & improves weed kill. Usually, directed spray is adopted with herbicides that are only partly selective to the treated crops.
- 3) **Protected spraying** :- In this method application of herbicide, non selective herbicides are applied in standing crop and ornamentals after physically covering the non-target plants with plastic or metallic covers. This method is used for treating high value wide

row crops only. If the soil condition do not permit use of inter cultivation implements or manual labour for weeding, this method can be followed.

- 4) **Spot treatment** :- Application of herbicide to a limited area such as a small patches or clumps of serious perennial weeds or weeds which were not controlled by previous cultivation or herbicide application. The object of spot treatment in crop field to avoid herbicide injury to crop plants, where as in non-cropped area it serves unnecessary wastage of toxicants in vacant spaces.

(c) Other methods of application :-

- 1) **Jar method** :- This method is suitable for treating deeprooted herbaceous perennial weeds growing under condition of extreme drought. The method comprises (a) Filling of glass jar with an appropriate herbicide solution such as 1% Arsenic solution and (b) Bending plant tops into their mouths. Under dry stress of water deficiency the shoots suck herbicide solution from jar & kills the weeds completely.
- 2) **Wax-box method** :- Herbicide laden soft wax box are available that can be dragged above the height of crop plant to rub against tall weeds. In this process some wax containing toxicants is left on the shoots to effect phototoxicity. 2, 4-D is applied successfully by this method for controlling certain tall growing broad leaved weeds in soyabean & lawns.
- 3) **Herbicide mulching** :- Cloth impregnated with weed killers have been developed. Its cut to fit the area to be treated & either anchored in places of surface or covered with a thin layer of soil. Rain or irrigation water transferred the herbicide to ground. The cloth decomposes before the end of growing season.

Assignment :-

1. Draw well labeled diagram of different methods of herbicide application..
2. Demonstrate the following methods on college field
 - i) Surface application
 - ii) Band Method
 - iii) Blanket application
 - iv) Spot treatment
3. Calculate labour unit / ha. For different methods demonstrated.

EXERCISE NO.15

STUDY OF PHYTOTOXICITY SYMPTOMS OF HERBICIDE IN DIFFERENT CROPS

Object :- To study toxicity symptoms of herbicide in different crops.

Sometimes herbicides are found to be carried over from one crop season to the next, however, it occurs in a few cases only. Sensitive crops in rotation are found to be damaged and in some cases the stand of the succeeding crop is found to be low or it is completely lost. For example application of atrazine and simazine in maize causes toxicity to cereals, soybean, cucumber and cotton. In paddy Butachlor as well as thiobencarb appear promising though they exhibit phytotoxicity causing stand reduction.

SUSCEPTIBILITY OF CROPS TO CERTAIN HERBICIDES

Herbicides	Susceptible crops
Barban	Oat, rye
Chlorbromuron	Sugar beet, cole crops, cucurbits, tomato, okra, rice
Chloroxuron	Sugar beet, cole crops.
2, 4-D (amine)	Dicot plants
2, 4-DEP (falone)	Cotton tobacco, tomato, onion, grapes
Dicamba	Soybean, beans, small assded legumes, ornamentals.
Dinoseb	vegetables
Flumeturon	Cruciferous crops
Fluorodifen	Sugar beet, cole crops, cucurbits, brinjal.
Metribuzine	Sugar beet, cucurbits, tomato, alfalia
Nepatalam	Sugar beet, cole crops, cruciferous crops, onion, pea, sunflower, sweet-potato, cotton and spinach
Picloram	Sugar beet, tomato, spinach
Propazine	Broad leaved plants except cruciferous crops
Simazine	Sugar beet, vegetables
TCA	Sugar beet, vegetables, tobacco
	Cereals and millets

Table: Effect of herbicide residue on the succeeding crop

Crop	Herbicide	Dose (kg/ha)	succeeding crop	
			Toxic	Nontoxic
Sunflower	Trifluralin	1.5 to 2.5	Wheat	--
wheat	2, 4 D Na	0.8	--	Cotton
	2, 4 D amine	0.8	-	Cotton
	2, 4 D ester	0.8	-	Cotton
Maize	Atrazine	5.0	Wheat	
	Simazine	5.0	Greengram	
cotton	Diuron	2.0 to 4.0	Wheat, sorghum	
			Chickpea	
Rice	Oxyflourfen		--	Chickpea
	Bentazone		Field beans	
sorghum	Atrazine	1.5	cowpea	--

Study of phytotoxicity symptoms of 2,4-D and Atrazine in cotton and soybean

Procedure :-

- Fill the earthen pots with soil Or prepared a seed bed of 2 m x 2 m.
- Sow the seeds of cotton and soybean in pots or on seed bed.
- Apply different concentration of 2,4-D and Atrazine in cotton and soybean respectively.

Observations:

- Observe toxicity symptoms of 2, 4-D and Atrazine on cotton and soybean plant respectively.

EXERCISE NO.16

HANDLING AND STORAGE OF FUNGICIDES AND AGROCHEMICALS

EXERCISE NO.17

PREPARATION OF BORDEAUX MIXTURE AND BORDEAUX PASTE AND FUNGICIDES

SOLUTIONS

Object: To know the methodology of preparation of fresh fungicides from copper sulphate/copper carbonate.

Most of the fungicides in use are commercially available as wettable powders and emulsifiable concentrates and few as seed dressers. However, some of the fungicides are to be prepared freshly every time as commercial formulations are not usually available. Moreover, the fungicides, which are unstable and lose the efficacy in storage are usually prepared freshly and applied to the crops. Some of the fungicides, which are most commonly prepared are given below.

1. Bordeaux mixture

In 1882, Millardet in France (Bordeaux University) accidentally observed the efficacy of the mixture of copper sulphate and lime against the downy mildew of grapes caused by *Plasmopara viticola*. When copper sulphate was mixed with lime suspension, it effectively checked the disease incidence. The mixture of copper sulphate and lime was named as "Bouillie Bordelaise" (Bordeaux mixture). The original formula developed by Millardet contains 5 lbs of CuSO_4 + 5 lbs of lime + 50 gallons of water. The chemistry of Bordeaux mixture is complex and the suggested reaction is: $\text{CuSO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{Cu}(\text{OH})_2 + \text{CaSO}_4$

The ultimate mixture contains a gelatinous precipitate of copper hydroxide and calcium sulphate, which is usually sky blue in colour. Cupric hydroxide is the active principle and is toxic to fungal spores.

In metric system, to prepare one per cent Bordeaux mixture the following procedure is adopted:

One kg of copper sulphate is powdered and dissolved in 50 litres of water. Similarly, one kg of quick lime is dissolved in another 50 litres of water. Then, copper sulphate solution is slowly added to lime solution with constant stirring or alternatively, both the solutions may be poured simultaneously to a third container and mixed well.

The ratio of copper sulphate to lime solution determines the pH of the mixture. The mixture prepared in the above said ratio gives neutral or alkaline mixture. If the quality of the used lime is inferior, the mixture may become acidic. If the mixture is acidic, it contains free copper which is highly phytotoxic resulting in scorching of the plants. Therefore, it is highly essential to test the presence of free copper in the mixture before application. There are several methods to test the neutrality of the mixture, which are indicated below:

- i) Field Test: Dip a well polished knife or a sickle in the mixture for few minutes. If reddish rusty deposit appears on the knife/sickle, it indicates the acidic nature of the mixture.

- ii) Litmus paper test: The colour of blue litmus paper must not change when dipped in the mixture. If it changes to red, indicates acidic pH.
- iii) pH paper test : If the paper is dipped in the mixture, it should show neutral pH on the colour indicator strip.
- iv) Chemical test: A few drops of the mixture are added into a test tube containing 5 ml of 10% potassium ferrocyanide. If red precipitate appears, it indicates the acidic nature of the mixture.

If the prepared mixture is in the acidic range, it can be brought to neutral or near alkaline condition by adding some more lime solution into the mixture.

Bordeaux mixture preparation is cumbersome and the following precautions are needed during preparation and application.

- i) The solution should be prepared in earthen, wooden, or plastic vessels. Avoid using metal containers for the preparation, as it is corrosive to metallic vessels.
- ii) Bordeaux mixture should be prepared fresh every time before spraying. In case, the mixture has to be stored for a short time or a day, jaggery can be added @ 100kg/100 litres of the mixture.

Merits of Bordeaux mixture

1. It is used in controlling wide variety of diseases, e.g., downy mildew, and anthracnose of grapes, betel vine wilt, late blight of potato, etc.
2. It is relative cheap.
3. It is having natural tenacity
4. Safety to handle

Demerits of Bordeaux mixture

1. It is troublesome to prepare
2. It has corroding action on metallic containers and spraying equipments.
3. It stains the fruits and reduces the market value.
4. Deteriorates on standing / storage.
5. It is phototoxic on certain crops like apples, peaches, etc.
6. Tendency to delay the ripening of fruits.

2. Bordeaux paste

Bordeaux paste consists of same constituents as that of Bordeaux mixture, but it is in the form of a paste as the quantity of water used is too little. It is nothing but 10 per cent Bordeaux mixture and is prepared by mixing 1 kg of copper sulphate and 1 kg of lime in 10 litres of water. The method of mixing solution is similar to that of Bordeaux mixture. It is a wound dresser and used to protect the wounded portions, cut ends of trees, etc. against the infection by fungal pathogens.

3. Cheshunt compound

Bewley suggested this compound in 1921. It is a mixture of 2 parts of finely ground copper sulphate and 11 parts of ammonium carbonate. Both ingredients are powdered and thoroughly mixed and dry mixture is stored in an airtight container for 24 hours before using, as it loses NH_3 and becomes less effective. Thirty g of mixture is dissolved in little quantity of hot water and volume is made up to 10 litres with cold water. It is used to drench nursery beds for control of "Damping off" diseases. Usually 30 g in a litre of water is used for soil drenching to manage soil borne diseases.

4. Chaubattia paste:

This paste was developed at the Government Fruit Research Station, Chaubattia, in the district of Almora of the Uttar Pradesh. It is prepared by mixing copper carbonate (800 gm) and red lead (800 gm) in 1 litre of lanolin or raw linseed oil. These are mixed in some glass or chinaware pot. This was developed as a wound dressing fungicide to be applied to pruned parts of apple, pear, and peach trees for the control of diseases like stem-black (*Coniothecium chomatosporum*), stem-brown (*Botryosphaeria ribis*), pink disease (*Corticium salmonicolor*), and stem canker (*Monochaetia mali*) of apple and pear, and collar rot (*Rosellinia* sp.) of apple, peaches, apricots, and plums. The paste has the advantage that it is not washed off easily by rain hence, advocated in high rainfall areas.

Exercise:

1. Prepare Bordeaux mixture 0.5 and 1.0 per cent concentration, test their pH by various methods and use for control of any severe fungal disease appearing on important crop and record the observations.
2. Prepare Bordeaux paste and Chaubattia paste and use them as wound dressing fungicides or apply on diseased portions of gummosis or stem bleeding of citrus, mango, coconut, cashew, etc. and note the disease control.
3. Prepare Cheshunt compound and use it for controlling the damping off of seedlings in the nursery.

EXERCISE NO.18

METHODS OF APPLICATION OF FUNGICIDES I (Foliar application)

Object: To know about different methods of application of fungicides on the foliage of plants.

Proper selection of a fungicide and its application at the correct dose and at the proper time are essential for the effective management of plant disease. In the application method, the fungicide is delivered to the target (plant parts) where the active ingredient acts.

The fungicidal application varies according to the nature of the host part diseased and nature of survival and spread of the pathogen.

Foliar application

i. Spraying

This is the universal method to apply fungicides on the foliage. Spraying of fungicides is done on leaves, stems, inflorescence and fruits. Spraying gives better coverage on the plant surface. Loss due to drift and pollution risk is very less. It has long residual effect. Spraying can be done at relatively high wind velocities. Spraying leads to less hazards to the operators than dusting. Wettable powders and emulsifiable concentrates are commonly used for preparing spray solutions. The most common diluent or carrier is water. The dispersion of the spray is usually achieved by its passage under pressure through nozzle of the sprayer. The amount of spray solution required for a hectare of land depends on the nature of crops to be treated. For trees and shrubs, more amount of spray solution is required. Depending on the volume of fluid used for coverage, the sprays are categorized into high volume, medium volume, very low volume and ultra low volume (ULV).

The spraying is done with the help of knapsack, power sprayer, HTP, etc.

Type of Spray	Quantity of spray solution required (litre /ha)	
	Ground crops	Orchard crops / Trees
High volume	700	1200
Medium volume	400 to 700	800 to 1200
Low volume	225 to 400	350 to 800
Very low volume	60 to 225	250 to 350
Ultra low volume	20	50

Preparation of spray solution

Usually Wettable powders or emulsifiable concentrates are diluted with water and the resultant solution is used for spraying. A known quantity of the fungicidal formulation is taken in a container to which a small quantity of water is added and mixed. Then the required quantity of water is added to make the required concentration and stirred well. It is taken in the sprayer and applied either in the morning or in the evening. For crops, which have glossy leaf surface (banana) or hairy leaf surface (sugarcane, rice, etc) spreading agents like soap (*khadi* soap at 1 g/litre of spray solution) or sticker (1 ml/litre) is added in the spray solution. The required concentration of the fungicide should be prepared. If it is less than the required concentration the targeted disease is not effectively controlled and if it is more, the chemical may cause phytotoxicity to the crop. Generally the following concentrations are used for the management of plant diseases.

Fungicide	Concentration recommended	Chemical required per one litre of water
Propiconazole	0.05%	0.50 ml/g
Carbendazim	0.1%	1.0g
Mancozeb	0.2%	2.0g
Copper oxychloride	0.25%	2.5g
Wettable sulphur	0.3%	3.0g

Requirement of Chemical

For spraying one acre of field crop generally 200 litres of spray solution (500 litres/ha) is required. The requirement of chemical for this area varies with the concentration of the solution and number of sprayings recommended. E.g., for two spraying in 2.0 ha of crop area with carbendazim (0.1%), the following is the calculations for the fungicide requirement.

Carbendazim 1 g/litre of water 0.1%

Hence, 500 g/500 litre of water/ha 0.1%

For 2.0 ha. $2 \times 500 \text{ L. of water}$ 1000 g/2ha for one spray.

For two sprays $1000 \text{ g} \times 2$ 2000g

Hence, 2.0 kg of carbendazim is required for two sprays on two ha area.

ii. Dusting

Dusting requires less labour for the operation. Dusting covers more area in a day than with spraying. Dusting equipments are lighter in weight and there is less risk of corrosion. Dusts are applied to all aerial parts of a plant as an alternative to spraying. Dry

powders are used to cover the host surface. Generally, dusting is practiced when the plant surface is wet with dew or raindrops. It is made during early hours in a day. Dust is applied @ 25 kg/ha. e.g., sulphur dust to control powdery mildew diseases of different crops in rainfed areas. The equipments employed for the dusting operation are bellows duster, rotary duster, motorized knapsack duster and aircraft.

Exercise:

1. Prepare 0.2 and 0.3 per cent solutions of copper oxychloride for spraying.
2. Prepare 100 ppm streptomycin solution for spraying

METHODS OF APPLICATION OF FUNGICIDES II

(Seed treatment and soil application)

Object: To know about different methods of seed treatment and soil application of fungicides.

I) Seed treatment with chemicals

The seed treatment with fungicides is essential since the pathogens are carried on or in the seed. Seed treatment protects the germinating seeds and growing seedlings from soil-borne pathogens. Seed treatment is an effective and economic method of disease control. Seed treatment is therapeutic when it kills pathogens that infect embryos, cotyledons or endosperms under the seed coat, eradicated when it kills pathogens that contaminate seed surfaces and protective when it prevents penetration of soil-borne pathogens into the seedlings.

Using fungicides on seed is one of the most efficient and economical method. Seed treatment chemicals may be seed disinfectant or seed protectant.

Seed disinfectant: Seed disinfectant, disinfects the seed but may not remain active for a longer period after the seed has been sown.

Seed protectant: Seed protectant, disinfects the seed surface and stick to the seed surfaces for sometimes after the seed has been sown, and thus giving temporary protection to the young seedlings against soil-borne fungi. Systemic fungicides disinfect the deep-seated infections in the seed.

The seed dressing chemicals may be applied by

- a. Dry seed treatment
- b. Wet treatment
- c. Slurry

a. Dry seed treatment

In this method, the fungicide adheres in a fine form on the surface of the seeds. A calculated quantity of fungicide is applied and mixed with seed using machinery specially designed for the purpose. The fungicides may be treated with seeds of small lots using simple rotary seed dresser (seed treating drum) or of large seed lots at seed processing plants using grain-treating machines. Normally at field level, dry seed treatment is carried out in rotary seed treating drums, which ensures proper coating of the chemical on the surface of seeds. The little quantity of gum may be added for better adherence of chemical on the seed surface. Dry seed dressing method is also followed in pulses, cotton and oilseeds with the antagonistic fungi like *Trichoderma viride* at the rate of 4g/kg of seed.

Dry seed treatment in rice: Mix a required quantity of fungicide with the required quantity of seeds in a seed treating drum or polythene-lined gunny bag and mix

thoroughly to provide uniform coating of the fungicide over the seeds. Treat the seeds 24 hr prior to soaking for sprouting. Thiram, captan, carboxin, Tricyclazole, and carbendazim are treated at 2g/kg of seed.

b. Wet seed treatment

This method involves preparing fungicide suspension in water and dipping the seeds, seedlings, or propagative materials in it for a specified time.

Seed dipping in rice: Fungicidal solution is prepared by mixing any of the recommended fungicides viz., carbendazim or pyroquilon or tricyclazole at 2g/litre of water and seeds are soaked in the solution for 2 hrs. Drain the solution and keep the seeds for sprouting.

Seed dipping in wheat: Prepare 0.2% solution of carboxin (2g/litre of water), soak the seeds for six hrs, drain the solution and dry the seeds and use for sowing. It eliminates the loose smut pathogen, *Ustilago tritici*.

Seed dip/root dip: The seedlings of fruits and vegetables are normally dipped in 0.25% copper oxychloride (2.5 g/litre of water) or 0.1% carbendazim solution (1g/litre of water) for 5 to 10 minutes to protect against seedling blights and rots.

Rhizome dip: The rhizomes of cardamom, ginger and turmeric are treated with 0.1% Emisan solution for 20 minutes to protect them from the attack by the pathogens present in the soil.

Set dip/sucker dip: The sets of sugarcane and tapioca and suckers of pineapple are dipped in 0.1% Emisan solution or 0.1% carbendazim solution for 30 min.

c. **Slurry treatment (Seed pelleting):** In this method, chemical is applied in the form of a thin paste (active material is dissolved in small quantity of water) to the seed. The required quantity of the fungicide slurry is mixed to the specified quantity of the seed, so that during the process of treatment slurry gets deposited on the surface of seeds in the form of a thin paste, which later dries up. Seed processing units have usually slurry treaters, which mix the fungicide slurry with specified quantity of seeds before the seed lot is bagged.

Seed pelleting in ragi: Mix 2.5g of carbendazim in 40 ml. of water and add 0.5 g gum to the fungicidal solution. Add 2kg of seeds to this solution and mix thoroughly to ensure a uniform coating of the fungicide over the seed. Dry the seeds under shade and sow after 24 hr after treatment.

d) **Acid-delinting in cotton:** This treatment helps to kill the seed-borne fungi and bacteria in cotton. The seeds are treated with concentrated sulphuric acid @ 100 ml/kg of seed for 2-3 min. The seeds are then washed 2 or 3 times thoroughly with cold water and shade dried. After drying, they are again treated with captan or thiram @ 4g/kg of seed before sowing.

II) Soil application of chemicals

Chemical treatment of the soil is comparatively simple especially when the soil is fallow as the chemical is volatile and disappears quickly either by volatilization or decomposition. Soil treating chemicals should be non-injurious to the plants in the soil adjacent to the area where treatment has been carried out. Methods of soil treatment are

- a. Soil drenching b. Broadcasting c. Furrow application.
- d. Fumigation and e. Chemigation.

- a. **Soil drenching:** It is followed for controlling damping off and root rot infections at the ground level. Required quantity of fungicide suspension is applied per unit area so that the fungicide reaches to a depth of at least 10-15 cm. It is applied with water can or through sprayer after removing nozzle.
- b. **Broadcasting:** It is followed in granular fungicides wherein the pellets are broadcasted near the plant.
- c. **Furrow application:** It is done for the control of diseases where the direct application of the fungicides on the plant surface leads to phytotoxicity. For the control of powdery mildew of tobacco, sulphur dust is applied in the furrows and not on the foliage.
- d. **Fumigation:** Volatile (fumigants) toxicants such as methyl bromide, chloropicrin, formaldehyde and vapam are the best chemical sterilants for soil to kill fungi and nematodes. Soil fumigants penetrate the soil efficiently. Fumigations are normally done in nursery areas and in glass house. The fumigant is applied to the soil and covered by thin polythene sheets for 5 to 7 days and then removed. E.g., Formaldehyde is applied at 350 to 500 ml/m² (i.e. 40 to 50 ml formalin (36 - 40%) per litre of water and applied @ 8-10 l/m²). The treated soil is irrigated and used for sowing/transplanting two weeks after treatment. Vapam is normally applied on the soil surface and covered. Volatile liquid fumigants are also injected to a depth of 15 cm using soil injector guns. The fumigants are not applied in the standing crops as they are injurious to them.
- e. **Chemigation:** the fungicides are directly mixed in the irrigation water. It is normally practiced when sprinkler or drip irrigation system is followed in a field or garden.

Exercise:

1. Carry out the dry and wet seed treatments with captan or thiram @ 0.3 and 0.5 per cent to gram seeds.
2. Prepare 4.0 per cent solution of formalin and carry out the soil treatment following five square meter area of raised bed.
3. Apply fungicide to sugarcane sets.

METHODS OF APPLICATION OF FUNGICIDES III

(Post harvest and special methods)

Object: To know about different methods of fungicide application for increasing the self-life of fruits after harvesting.

I) Post harvest application

Fruits and vegetables are largely damaged after harvest mostly by fungi and bacteria. The use of chemical method is found to be economical and effective. Fumigation, dipping them in solutions and wrapping of the harvested products with fungicide impregnated waxed papers are the important methods adopted in control of post harvest diseases. Fumigation is followed in limited cases. Further fumigants with the desirable qualities like quick volatility, highly effective against microorganisms, non-phytotoxic and non-tainting in nature are very few. Commercial fumigant commonly used for this purpose is sulphur. In addition, tetrachloroethylene, dichloromethane, ammonia, nitrogen trichloride are also used as fumigants.

Dipping the fruits in fungicidal solution is better than in suspension. In suspension the fungicide deposits on the surface of fruits. E.g., sodium -D-naphthylphenate solution with 1% hexamine is suggested for oranges and apples. A dip in 0.1 - 0.2 per cent aqueous solution of dichloran (2,6-dichloro 4 nitro aniline) for 1 or 2 min is effective against *Rhizopus* rot of peaches.

Wrapping citrus fruits with waxed paper impregnated with diphenyl or phenylbenzene or lining the packing container with the paper are followed in fruit industry to avoid infection of *Penicillium*, *Botrytis*, *Rhizopus* spp. At present, post harvest treatment of fruits and vegetables with systemic fungicides like benomyl or thiabendazole is being practiced.

II) Special methods

i. Corm injection

Corm injection with the fungicide carbendazim is followed to control the dreadful disease of banana viz. Panama wilt (*Fusarium oxysporum* f.sp. *cubense*). Carbendazim is applied either in the form of 2 per cent solution or in the form of capsule.

ii. Capsule application method: Carbendazim 50% WP 50 to 60 mg is taken in a gelatinaceous capsule. The soil above corm in the banana tree is removed to expose the corm. A capsule applicator made of iron is employed to make a hole to apply the carbendazim capsule. Capsule applicator is made with 7 mm thickness iron rod. The length of the rod is 45 cm. One end of the rod is sharpened. An iron plate is fixed 7 cm above the pointed end for the purpose of inserting the rod at a constant depth of the corm. At the top of the iron rod, a wooden handle is fixed. The iron rod is inserted up to the iron plate into the exposed corm at an angle of 45° to make a hole

Carbendazim capsule is pushed to the hole and covered with clay soil. The corm is again covered with the removed soil.

iii. Application of carbendazim 2% solutions: Two per cent solution of carbendazim 50 WP is prepared by mixing 20 g of carbendazim in one litre of water. A whole in the banana corm is made by following the same method as described above for capsule application. Three ml carbendazim (2%) solution is injected into the hole through syringe and the hole is plugged with clay soil.

iv. Root feeding.

Root feeding with the antibiotic, Aureofungin-sol + copper sulphate is employed in the control of basal stem rot (Tanjore wilt or *Ganoderma* wilt) of coconut caused by *Ganoderma lucidum*. Tridemorph (Calixin) can also be used at 2ml/100ml water. It is an improved and effective method compared to trunk injection, which is an old and dangerous method, which may cause even copper sulphate death of the tree.

Methodology: One pencil thickness, active coconut root is selected and exposed outside from the soil by removing a layer of soil and is cut at a distance of 60 cm from the tree. A slanting cut is made at the tip to have more surface area for absorption. Root feeding chemical is prepared as follows:

Aureofungin-sol	- 1.3 g
Copper sulphate	- 0.5 g
Water	- 100 ml

Copper sulphate is powdered well and it is dissolved in 100ml of water along with the Aureofungin-sol. The solution is taken in a polythene bag. The tip of the root is inserted into the polythene bag containing 100 ml of the fungicidal solution. Later the mouth of the bag is tied tightly around the root keeping the cut end touching the bottom of the bag. The solution is normally absorbed within 24 hrs. If it is not absorbed in 24 hrs, another healthy root should be selected as done before and the root feeding is given. It is followed thrice in a year at every four months for effective control of the disease.

Exercises:

1. Prepare 0.05 and 0.10 per cent solutions of carbendazim, carry out fruit dip treatment and record the self-life of the fruits.
2. Prepare the solution of Aureofungin or Calixin as indicated above and do the root feeding exercise in coconut.
3. Prepare the capsules of carbendazim, apply to few healthy banana plants and record disease observations once at capsule application and second at one month after application.