CH-533: ANALYTICAL AND ENVIRONMENTAL CHEMISTRY

UNIT- II

The soil testing is essential due to the following factors.

- The soil fertility depends upon the availability of nutrient in soil. So the estimation of nutrient is essential.
- The determination of the availability of nutrient in the soil is essential in order to know the subsequent uptake of these nutrients by crop plant.
- The soil testing also determines the optimum application of fertilizer in soil.
- The soil testing also concern with environmental quality for the community hazards.

The soil fertility may be defined as the capacity of the soil to supply the available plant nutrients to the plants in proper amount and appropriate balance under ideal condition of plant growth.

The soil productivity is defined as the capacity of the soil to produce under specific condition of crop production.

The plant nutrients from the soil are divided into three types.

- ✓ Primary nutrients: Nitrogen, Phosphorous and Potassium -: N-P-K fertilizers
- ✓ Secondary nutrients: Calcium, Magnesium and Sulfate -: Lime [$Ca(OH_2]$, Gypsum ($CaSO_4$. $2H_2O$) and Sulfur fertilizer.
- ✓ Micro nutrients: Boron, Chlorine, Copper, Iron, Manganese, Molybdenum and Zinc. The micro nutrients are essential elements and found less than 0.01 % of the plant dry matter.

Estimation of Nitrogen

The total nitrogen present in soil or plant is estimated by micro-Kjeldahl method as per procedure suggested by AOAC (Association of Official Agricultural Chemists) in 1995.

Preparation of Plant and soil samples

Plant Analysis

The plant analysis has been considered as a superior diagnostic technique for mineral content. The whole plant is dried in open air for few days after that it is further dried in hot air oven at temperature of about 60 ± 2 ^oC for 8 to 10 hours per day to achieve

complete drying.After complete drying, the whole plant is powdered with the help of grinder. Then it is passed through 2 mm stainless steel sieve and used for chemical assay.

Soil Analysis

The soil sample from definite depth is randomly collected from the field with the help of screw auger. All the possible technical precautions are taken as prescribed for standard soil sampling. Samples are brought to the laboratory and air dried in shade. This dried soil is grounded by wooden roller followed by sieved through 2 mm stainless steel sieve. This is stored in polythene bags and used for chemical assay.

Principle:

The nitrogen in soil and plant samples exists in very complicated bonding structure. The known weight of plant or soil samples is digested in the presence of sulfuric acid with catalyst mixture under high temperature. During digestion the complicated bonding structure of nitrogen is converted to simple structure. During this period the nitrogen is released in the form of ammonium radical (NH_4^+). This released ammonia is condensed during distillation with sodium hydroxide. This condensed ammonia is absorbed in the known volume of boric acid with mix indicator. It is converted to ammonium borate, $(NH_4)_3BO_3$. The excess of which is titrated with standard sulfuric acid.

The micro-Kjeldahl method consists of the three steps.

(1) Digestion (2) Distillation (3) Titration

Equipment and apparatus:

(1) KEL PLUS Automatic Nitrogen Estimation System.

The KEL PLUS instrument is used for the determination of nitrogen. It consists of the following equipment.

- Macro Block Digestion System

This digestion system is suitable for soil, plant, water, pesticide, fertilizer, food and feed samples. It is microprocessor based automatic twelve place macro block digestion system. It is attached with temperature controller fitted with sensor break protection (Microprocessor based). The temperature range is from 50 – 450^{o}C.

- Acid Neutralizer Scrubber

It is used to neutralize the acid fumes. This is absorbed in 15 % NaOH and dissolved in water followed by stored in the system tank. The 15 % NaOH solution is replaced after every two cycles of digestion. The acid fume dissolved in water tank is drained off after every three cycles of digestion. The system tank is refilled with fresh water.

- Automatic Distillation System

It is fully automatic distillation system with programmable auto run digital feature. It has featured with automatic dilution and addition of boric acid and NaOH. Both modes (Auto and manual) are available for distillation reagent addition.

- Refrigerated water cooling system for condenser

It is refrigerated water cooling system for distillation and condensing system with inbuilt compressor and recirculate pump.

(2) Electronic balance (3) Burette (4) Pipette (5) Conical flask (6) Measuring cylinder (7) Distilled water

Reagents:

(1) Concentrated sulfuric acid (H_2SO_4)

(2) Catalyst mixture: It contains 250 g. (1.43 mol) potassium sulfate (K_2SO_4), 50 g. (0.2 mol) Cupric sulfate ($CuSO_4$. $5H_2O$) and 5 g. (0.06 mol) metallic selenium powder in the ratio of 50:10:1 by weight.

(3) 40 % sodium hydroxide solution (NaOH)

(4) 4 % boric acid (H_3BO_3) containing 20-25 ml. mixed indicator/liter.

(5) Mixed indicator: 0.066 g. (2.45×10^{-4} mol.) methyl red + 0.099 g. (1.83×10^{-4} mol.) bromocresol green dissolve in 100 ml. of 95 % alcohol.

(6) 0.02 N sulfuric acid (H_2SO_4)

Procedure:

I. Digestion

- The 0.5 g. prepared plant or 1.0 g. soil sample is weighted and transfers it to the digestion tube.
- 10 ml. of Conc. H_2SO_4 acid and 5 g. of catalyst mixture is added to the sample.
- The digestion tube is loaded into the digester and the digestion block is heated.

- The digestion unit is switched on and the initial temperature is set to 100°C till frothing is over.
- Then the block temperature is raised to 400°C. The effective digestion starts only at 360°C and beyond 410°C.
- The sample turns light green colour or colourless at the end of the digestion process.

II. Distillation

- The digestion tube is cooled and this tube is loaded in distillation unit. The 20 ml of 4 % boric acid with mixed indicator is kept in 50 ml conical flask and it is placed in other side of hose.
- The 40 ml of 40 % NaOH solution is added in thedistillation unit automatically due to programmable auto run digital feature.
- The digested sample is heated by passing steam at a steady rate and the liberated ammonia is absorbed in 20 ml of 4 % boric acid containing mixed indicator. The solution is kept in a 250 ml conical flask.
- The pinkish colour of the solution turns to green colour due to absorption of ammonia.
- In this process about 150 ml of distillate is collected in about 8 minutes.
- Simultaneously, the blank sample (without plant or soil) is to be run.

III. Titration

- The green colour distillate is titrated with 0.2 N sulfuric acid and the colour changes to original pinkish colour.
- The blank and sample titer reading is noted. The total nitrogen content in plant or soil sample is calculated.

Calculation:

$$Nitrogen\ content\ in\ plant(\%) = \frac{R(Sample\ titer - Blank\ titer) \times Normality of\ acid \times Atomic\ weight\ of\ nitrogen \times 100}{Sample\ weight\ in\ g. \times 1000}$$

$$Nitrogen\ content\ in\ plant(\%) = \frac{R \times 0.1 \times 14 \times 100}{0.5 \times 1000}$$

$$\boldsymbol{Factor = R \times 0.28}$$

$$Nitrogen\ content\ in\ soil(\%)$$

$$= \frac{R(Sample\ titer - Blank\ titer) \times Normalityof\ acid \times Atomic\ weight\ of\ nitrogen \times 100}{Sample\ weight\ in\ g. \times 1000}$$

$$Nitrogen\ content\ in\ Soil(\%) = \frac{R \times 0.1 \times 14 \times 100}{1.0 \times 1000}$$

$$\boldsymbol{Factor = R \times 0.14}$$

Crude protein content:

The total nitrogen is estimated by micro-Kjeldahl method as per procedure suggested by AOAC in 1995 and the crude protein is calculated by the following formula.

Crude protein content (%) = micro-Kjeldahl nitrogen content (%) × 6.25 (Based on the assumption that nitrogen constitutes 16 % of the protein)

Estimation of Phosphorous using Olsen et.al

The Phosphorous is an essential plant nutrient and it is available in many different forms such as Phosphates (PO_4^{3-}), monohydrogen phosphate (HPO_4^{2-}) and dihydrogen phosphate ($H_2PO_4^-$). These anions are readily inter-convertible. Therefore, a reliable procedure is required for the estimation of phosphorous in plants as well as in soils. The colorimetric method developed by Olsen et.al. in 1954 is the best among all other methods.

Principle:

The phosphorous is extracted from the soil using 0.5 M $NaHCO_3$ at a nearly constant pH of 8.5. The phosphate ion present in the solution is treated with ascorbic acid in an acidic medium. In this medium the solution is converted to blue colour complex. The quantitative determination of phosphorous is carried out using Olsen's et.al. method.

Deficiency of Phosphorous

- ✓ Phosphorous is a molecular component of genetic reproduction. In deficiency of phosphorous genetic process such as cell division and plant growth are impaired. Hence the phosphorous deficiency plants may mature at a slower rate than the plants with adequate amount of phosphorous.
- ✓ The deficiency of phosphorous has been correlated with smaller leaf sizes and a lessen number of leaves.

- ✓ This deficiency also causes the imbalance in the storage of carbohydrates. The photosynthesis also remains in normal rate.
- ✓ The deficiency is very difficult to diagnostic than the deficiency of nitrogen. By the time visual deficiency is recognized, it is too late to correct the annual crops.

Detection of phosphorous deficiency

- ✓ The darker green leaves and purplish or red pigment can indicate a deficiency in phosphorous.

Reagents:

- o 0.5 M sodium bicarbonate ($NaHCO_3$) solution: The 42 g. of $NaHCO_3$ is dissolved in one liter distilled water and the pH of the solution is adjusted to 8.5 using NaOH solution.
- o Activated charcoal: The phosphorous free Darco G-60 activated charcoal is used.
- o 5 N sulfuric acid (H_2SO_4) solution: The 141 ml of Conc. H_2SO_4 is added to 800 ml. of distilled water. The solution is cooled to room temperature followed by dilution with distilled water to 1 liter.
- o Reagent A: (i) The 12 g. (9.94×10^{-3}mol) of ammonium paramolybdate, $H_{66}Mo_7N_6O_{24}$, i.e. $(NH_4)_6Mo_7O_3.\ 21H_2O$,is dissolved in 250 ml. distilled water.

  (ii) The 0.2908 g. (4.35×10^{-4} mol) of potassium antimony tartrate, $K_2Sb_2(C_4H_2O_6)_2.3H_2O$, is dissolved in 100 ml. distilled water.

  (iii) Both the above solutions are mixed thoroughly made up to one liter solution in volumetric flask with the help of distilled water.

  (iv) The dissolved reagents are added to one liter 5 N H_2SO_4.
- o Reagent B: Ascorbic acid solution: The 1.056 g (5.99×10^{-3}mol) of ascorbic acid is dissolved in 200 ml. of reagent A and thoroughly mixed. The ascorbic acid should be prepared freshly due to its unstability.
- o Standard phosphate solution:

The 0.4393 g. (3.22×10^{-3} mol.) of potassium dihydrogen phosphate (KH_2PO_4) is weighted into one liter volumetric flask. The 500 ml of distilled water is added and it is continued to shake till all the salts are dissolved. The solution is diluted to 1(one) liter with distilled water in order to get 100 ppm P solution. Then 20 ml. of 100 ppm P solution is diluted to one liter in order to get 2 ppm solution.

Preparation of standard curve:

- The different amount of 2 ppm standard P solution such as 0, 1, 2, 3, 4, 5, etc. ml, is taken in 25 ml volumetric flask in order to get different concentration of P solution.
- The 5.0 ml of 0.5 M $NaHCO_3$ extracting solution is added in each flask followed by acidify with 5 N H_2SO_4 drop by drop.
- Then 10 ml. distilled water and 4 ml. of reagent B is added then the solution is continues to shake. The volume is made up to 25 ml through distilled water.
- The intensity of the blue colour is noted using spectrophotometer at 660 nm wavelength after 10 minutes.
- The curve is plotted by taking P concentration on X-axis and colorimetric reading on Y –axis. This process is repeated till a straight line is observed.
- The factor is calculated i.e. 1 colorimeter reading = X ppm of phosphorous.

Procedure:

- The 2.5 g. of soil sample is taken in 150 ml conical flask and 0.5 g. Darco G-60 activated charcoal is added.
- Then 50 ml. of 0.5 M $NaHCO_3$ solution is added followed by shaking the solution for 30 minutes in a shaker. The similar process is carried out for a blank sample i.e. without soil.
- The suspension solution is filtered through Whatman no. 40 paper.
- The 5.0 ml. of aliquot of the extract is taken in 25 ml. volumetric flask and acidify with 5.0 N H_2SO_4.
- The small quantity of the distilled water is added followed by the addition of 4.0 ml of reagent B.
- The intensity of the blue colour is noted on spectrophotometer at 660 nm wavelength after 10 minutes.

Observations:

Weight of the sample: 2.5 g.

Volume of extractant used: 50 ml.

Volume of filtrate used: 5.0 ml.

Absorbance : R

Absorbance from standard curve : A

Concentration of P for absorbance A : B ppm.

Calculation:

$$Available\ Phosphorous\ (kg\ ha^{-1}) = \frac{R \times F \times 50 \times 2.24}{5 \times 2.5} \quad ; \quad Where, F(factor) = B/A$$

Estimation of Phosphorous using Bray-Kurtz test

Dr. Bray and Dr. Kurtz was developed a method for the estimation of phosphorous present in soil in 1945 at the University of Illinois. This method is called as Bray-Kurtz P1 test. Sometimes it is also referred to as Bray-P1 test. This test is suitable for acidic (pH < 7.0) and neutral soils (pH = 7.0) but it fails for alkaline soils (pH > 7.0).

Principle

Phosphorus is extracted from the soil using Bray No 1 solution. The extracted phosphorus is measured quantitatively using colorimeter. This is based on the reaction with ammonium molybdate[$(NH_4)_2MoO_4, mol.wt.196.01\ g.$]which develops Molybdenum blue colour. The absorbance intensity of thiscolourcompound ismeasured at 882 nm in a spectrophotometer which is directly proportional to the amount ofphosphorus extracted from the soil.

Apparatus required

- Centrifuge (6 000 rpm).
- Diluter/Dispenser (Brand Diluette® Cat No 7046 54).
- High strength centrifuge tubes with caps (15 ml capacity).
- Spectronic 20 photometer with 10 ml. tubes.

Reagents

✓ Bray No 1 Extracting Solution

The 2.22 g. of ammonium fluoride A. R. (NH_4F) is dissolved in deionised water and transferred to a 2.0 lit.volumetric flask. Then 5 ml of Conc. HCl is added and made up to volume with deionized water.

✓ Reagent A

The 17.14 g. ammonium molybdate A.R. [$(NH_4)_6Mo_7O_{24}.4H_2O$] is dissolved in 200 ml of warmdeionised water. The 0.392 g. potassium antimony tartrate A.R. $K_2Sb_2(C_4H_2O_6)_2.3H_2O$ is dissolved separately in 150 ml deionised water. The 500 ml.deionised water is placed in a 2 lit.volumetric flask followed by addition of 200 ml.Conc.H_2SO_4slowly with constant stirring. This solution is cooled to room temperature followed by addition of ammonium molybdate and potassium antimony tartrate solutions. These are thoroughly mixed and made up to volume with deionised water.

- ✓ Reagent C

The 0.53 g. L-Ascorbic Acid A.R. ($C_6H_8O_6$) is dissolved in deionised water and transferred to a 500 ml volumetric flask. The 70 ml. of Reagent A is added and made up to volume with deionised water. The fresh solution is always prepared for the above experiment.

- ✓ Standard Phosphorus Solution (P ≡ 50 mg/lit.)

The 0.2195 g. potassium dihydrogen orthophosphate A.R. (KH_2PO_4) is dissolved in 100 ml. deionized water and transferredit to a one liter volumetric flask. Then5 ml. of Conc.H_2SO_4 acid (A.R.) is added and made up to volume with deionized water.

- ✓ Phosphorus Working Standard (P ≡ 2.50 mg/lit.)

The 5.0 ml. standard phosphorus solution is pipetted into a 100 ml. volumetric flask and made up to volumewith deionised water.

Procedure

- ✓ The 7.0 ml. of Bray Extracting Solution is dispensed into the oven-dry equivalent of 1 g of air-dry soil contained in a centrifuge tube. One tube is also included containing the Bray Solution only for the blank.
- ✓ The tube is stoppered and shacked vigorously for 1 minute.
- ✓ The tubes are transferred to the centrifuge and spin at 6000 rpm for 5 minutes.
- ✓ The 0.50 ml. of the supernatant plus is dispensed into 2.0 ml of Reagent C into a colourimeter tube. Both the solutions are thoroughly mixed and kept stand for 30 minutes.
- ✓ The reference standards are prepared from the 2.50 mg/lit.phosphorus solution using diluter/dispenser.

Table 1

DILUTION TABLE FOR STANDARDS			
mls 2.5mg/L Ref.	mls Reagent C	Phos. Conc. (µg/2.5 mL)	Typical Absorbance Value
0.05	2.45	0.125	0.06
0.10	2.40	0.250	0.09
0.20	2.30	0.500	0.17
0.30	2.20	0.750	0.26
0.40	2.10	1.000	0.34
0.50	2.00	1.250	0.40

- ✓ The instrument is set to zero (∞ Abs.) and then set full scale (zero Abs.) using the blank solutionprepared above.
- ✓ The absorbance of the standards and samples at wavelength 882 nm is measured and recorded.
- ✓ A chart or graph from the standards data is prepared to plot phosphorus concentration againstabsorbance or derive the equation of the line of best fit using linear regression. The phosphorous concentration in the sample solution is determined using the chart or equation.

Calculations

Calculate Available Phosphorus content.

$$Available\ phosphorous\left(\frac{mg}{kg}\right) = \frac{C \times 14}{ODW}$$

Where:

C = Phosphorus concentration from chart/equation (µg/2.5 ml.)

ODW = Oven-dry sample weight (g.)

14 = Dilution factor

Exchangeable Calcium & Magnesium (by EDTA)

Reagents

- ✓ 40 % ethanol.
- ✓ **1N Ammonium Acetate Solution (NH_4OAc)**: The 57 ml. of concentrated acetic acid (CH_3COOH) is added to 800 ml distilled water. Then the 68 ml. concentrated ammonium hydroxide (NH_4OH) is added to it followed by thoroughly mixed and the mixture is

cooled.The mixture is adjusted to pH 7.0 by adding more acetic acid or ammoniumhydroxide. Themixture is made up to volume 1.0 liter with distilled water.

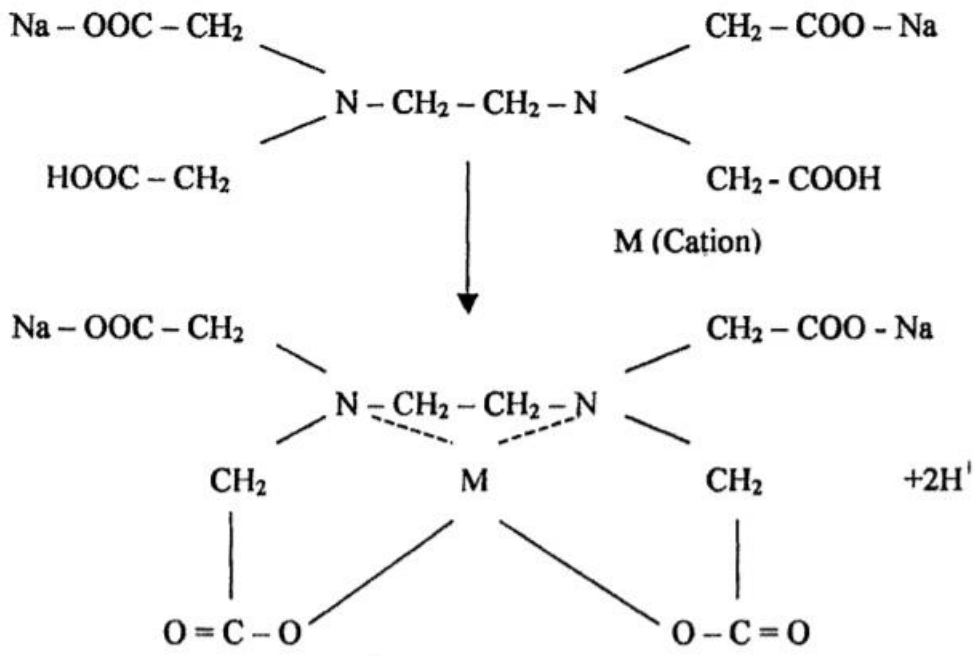
- ✓ **Aqua regia**: It is prepared by combining three parts of Conc. HCl to one part of Conc. HNO_3 in a glass container. The hydrochloric acid must be measured into the glassware first and then the nitric acid is slowly added. The HNO_3 should not exceed more than 38%.
- ✓ **Buffer solution of NH_4Cl and NH_4OH**: It is prepared by dissolving 67.5 g. of ammonium chloride (NH_4CI) in 200 ml. of distilled water followed by addition of 570 ml. of concentratedammonium hydroxide (NH_4OH). Then the solution is diluted to a volume of 1 liter with distilled water.
- ✓ **0.01 N EDTA solution**: The 1.8613 g. of disodium ethylenediaminetetraacetate (EDTA) (molecular weight = 336.21 g.) is dissolved in distilled water and dilute the solution to a volume of 1 liter. This solution is 0.005 molar. Its titer will change if stored in glass containers but not in polyethylene.
- ✓ **Eriochrome Black T. indicator**: The 0.2 g. of Eriochrome Black T. (EBT) is dissolved in 50 ml. of methanol. The fresh solution is prepared in every 3 weeks.

Complexometric titration:

The most widely used method for the determination of Ca and (Ca + Mg) is by complexometric titration involving ethylenediaminetetraacetic acid (EDTA). This is first introduced by Schwartzenbach et al. (1946). EDTA exhibits strong complexing power with metal ions including alkaline earth metals in an order depending upon the dissociation constant of the complex. In other words, EDTA forms a stable metal complex with many metals at different pHs.The disodium salt of EDTA with the formula $Na_2H_2Y.2H_2O$, where Y is the tetravalent anion of EDTA was used in the titration. When Ca^{2+} is treated with H_2Y^{+2}, a very stablecomplex isformed. The generalized reaction of EDTA with Ca^{2+} ion is shown below:

$$Ca^{2+} + H_2Y^{+2} \rightarrow CaY^{+2} + 2H^+$$

Mg^{2+} ion forms a similar complex, MgY^{+2}, which is far less stable than the Ca-complex. The characteristic reaction showing the complex formation of EDTA with a metal cation M is as follows [Hesse, 1971].



Preparation of the Ammonium Acetate extract.

The 50 g of the air-dried sample was treated with 40 % alcohol and filtered through Whatman No. 50 filter paper. The soil was washed 4-5 times with 50 ml portion 40 % alcohol. Then the soil was treated with 100 ml 1.0 N NH_4OAC solution and kept it for overnight. The suspension was filtered through Whatman No. 42 filter paper and the volume was made up to 500 ml withdistilled water. A portion of the NH_4- acetate extract was evaporated to dryness to eliminate the interference of organic matter. The residue was dissolved in aqua regia. Again, it was evaporated to dryness. This time the residue was dissolved in distilled water to make up the original volume of the extract evaporated.

Estimation of Calcium and magnesium.

The 50 ml. of the aliquot was taken in a conical flask. 1ml of thebuffer solution (NH_4CI - NH_4OH) and 100 mg. of Eriochrome Black T indicator wereadded. The wine red solution was titrated with 0.01 N EDTA solution till the colourchanges to blue.

Estimation of Calcium:

The 50ml. of the aliquot was taken in a conical flask. 2.0 ml of 10 % NaOH solutionand 100 mg.murexide (ammonium purpurate) indicator were added. The pink coloursolution was titrated with 0.01 N EDTA solution until the pink colour changes to darkpurple.

Calculation:

$$Ca\left(\frac{m_{eq.}}{kg}\right) = \frac{A \times 400.8 \times V}{v \times 20.04 \times S} \quad ; \quad Mg\left(\frac{m_{eq.}}{kg}\right) = \frac{(B - A) \times 400.8 \times V}{v \times 1.645 \times S \times 12.16}$$

Where, A = volume of EDTA (ml) used for Ca^{2+} determination

B = Volume of EDTA (ml.) used for Ca + Mg determination.

V = Total volume of soil extract prepared (500ml)

v = Volume of the soil extracts titrated (50ml)

S = weight of the soil sample (50 g).

Soil analysis for Micronutrients

Boron: It is important in cellular functions and for pollen germination and growth. It is also essential for seed and cell wall formation.

Iron: It is important for electron transport in some enzymes and also associated with enzymes in chlorophyll formation.

Copper: It is a constituent of oxidase enzymes. It is a component of some protein (helps with electron transfer).

Manganese: It accelerates the germination and maturity. It is also indirectly related to chlorophyll formation. It is involved in oxidation / reduction in photosynthesis.

Molybdenum: It is important component of legume nodules.

Zinc: It improves root development, flowering and fruit production. It is also need for producing chlorophyll.

These micronutrients are available from dead plant tissues or manure application. The organic matter may breakdown and release micronutrients. In case of acid soils, the micronutrients have removed due to leaching.

Prevention of contamination:

In order to avoid contamination, the soil samples are collected in plastic tub. The used instrument should be rust free or made up of wood. The soil samples are kept in polythene lined cloth bags. The samples are prepared with the help of wooden morter and pastle. These samples are sieved through 2 mm nylon screen or mosquito net cloth or stainless steel sieve.

Soil extraction:

The micronutrients such as Zn, Cu, Fe, Mn, Cd, Ni, Pb etc. undergo complex formation with DTPA (Diethylenetriaminepenta acetic acid) (Lindsay and Norvell, 1978). The extractant is buffered in a slightly alkaline pH range 7.3 by including soluble Ca^{2+} ions. The $CaCO_3$ dissolution is avoided because it releases the occluded micronutrients due to CO_2 partial pressure which is approximately 10 times than that of atmosphere. The soil contains slightly higher CO_2 levels than found in the atmosphere.

- ✓ **Extracting solution**:1.9679 g.(0.005 M) of DTPA and 13.3 ml. of TEA (Triethanol amine) followed by 1.47 g. $CaCl_2$. 2 H_2O is dissolved in 200 ml. distilled water. This solution is diluted to 900 ml. with distilled water. The pH of the solution is adjusted to 7.3 using 6.0 N HCl with stirring followed by made up to volume 1.0 liter. The solution is thoroughly mixed.
- ✓ **Apparatus required**: (1) Shaker (Horizontal or Rotatory), (ii) Iodine value flasks (100 ml. capacity) or conical flask with glass stoppers, (iii) Funnels, (iv) Filter paper Whatman No.1 (v) Plastic storage bottles (vi) Atomic Absorption Spectrophotometer.
- ✓ **Stock Standard Solutions**: The standard solutions of different micro-nutrients should be prepared by using their wires. The 1 g. of individual wire is dissolved in a minimum volume of 1:1 nitric acid followed by dilution with 1000 ml. using distilled water in order to obtain 1000 µg/ml. solution of micro-nutrient. The metal salts can be considered instead of wire as follows.

  Zn : 4.398 g. $lit.^{-1}$ ($ZnSO_4$. $7H_2O$) ; Cu : 3.929 g. $lit.^{-1}$ ($CuSO_4$. $5H_2O$)

  Fe : 4.977 g. $lit.^{-1}$ ($FeSO_4$. $7H_2O$) ; Mn : 3.598 g. $lit.^{-1}$ ($MnSO_4$. H_2O)
- ✓ **Soil analysis**: The 12.5 g. soil sample is weighted in 100 ml. iodine value flasks. The 25 ml. of DTPA solution is added in it. The mixture is shaken for 2 h. on shaker at 70 to 80 oscillations per minute. The solution is filtered in Whatman No.1 filter paper. This filter paper is washed with acid followed by rinsed in distilled water. The filtrate is collected in plastic bottles. The micronutrients are determined using Atomic Absorption Spectrophotometer.

Estimation of Propiconazole:

Propiconazole residues are extracted from soil with a mixture of methanol and water. The filtered extract is diluted with water and saturated sodium chloride solution. The propiconazole is partitioned into dichloromethane. The dichloromethane extracts are rotary-evaporated to dryness. The residue is cleaned up by column chromatography on aluminium oxide.

Apparatus:

[1] High speed blender fitted with leak-proof glass jar and explosion proof motor.

[2] Homogenizer.[3] Wide neck bottle, 500-mL with ground stopper.

[4] Laboratory mechanical shaker, [5] Buchner procelaen funnel, 9 cm dia.

[6] Filter paper, 9 cm dia, e.g. Macherey-Nagel No. 713, [7] Filtration flask, 1-L,

[8] Separatory funnel 1-L,

[9] Round bottom flasks, 300 mL, 100 mL and 25 mL with ground joints.

[10] Rotary vacuum evaporator, 40 °C bath temperature, [11] Test tubes, 10 mL with ground stoppers, [12] Glass syringe, 10 mL with Luer lock fitting.,

[13] Chromatographic tube, 20 mm i.d. 30 cm long.

[14] GC equipped with thermionic nitrogen specific detector, [15] Micro-syringe, 10 µL

Reagents:

[1] Cyclohexane, [2] Dichloromethane, [3] Ethanol , [4] Ethyl acetate , [5] n-hexane

[6] Methanol (high purity), [7] Toluene, [8] Cyclohexane : ethyl acetate mixture (1:1 v/v)

[9] **Eluting mixture 1**:dichloromethane : n-hexane (4:6 v/v)

[10] **Eluting mixture 2**:dichloromethane : n-hexane (6:4 v/v),

[11] Ethanol : n-hexane mixture (1:1 v/v); [12] Methanol : water mixture (8:2 v/v) ,

[13] Propiconazole standard solutions; 0.25, 0.5, 1.0 and 10.0 g/ml. in ethanol hexane mixture

[14] **Sodium chloride solution saturated Aluminium oxide, activity grade V**: The 19 ml. water is added drop wise from a burette with continuous swirling to 100 g. Alumina Woelm B Super I (ICN Biomedicals) in a 300 mL Erlenmyer flask (with ground joint), add. Immediately,the flask is stopperedwith ground stopper and shakes vigorously until all

lumps have disappeared.Then it is stored in a tightly stoppered container for at least 2 h., 200-400 mesh.

[15] Dry ice, [16] Cotton wool, [17] Compressed air, dried and re-purified,

[18] Hydrogen, re-purified, [19] Nitrogen, re-purified.

Procedure:

(a) **Extraction**: The 10 g of the soil sample is weighted into a wide neck bottle. The 200 ml. methanol-water mixture is added in samples of soil.The bottle is tightly stoppered and shook for 1 h. on a mechanical shaker followed by suction-filter through a Buchner porcelain funnel. The filter cake is washed with two 25 ml. portions of methanol. The filtrate is transferred to a separatory funnel. The 200 ml. water and 50 ml. sodium chloride solution is added and extracted three times with 75 ml. portions of dichloromethane. The dichloromethane phase is filtered through a cotton wool plug into a 300 ml. round bottomed flask and rotary-evaporate to dryness. The water phase is discarded. The residues is further proceeded for cleanup.

Column chromatography:

The 15 ml. hexane is poured into the chromatographic tube. The 30 g. of Aluminium oxide is slowly added (free from air bubbles). It is allowed to settle and then drained the hexane to the top of the column packing. The residue is transferred to column using three 2 ml. portions of toluene to complete the transfer. The toluene is drained to the top of the column packing each time. The co-extractives is eluted with 50 ml. of eluting mixture 1 and then eluted propiconazole with 75 ml. of eluting mixture 2 using a flow rate of 1 to 2 drops per s. The elute is collected in a 100 ml. round bottomed flask and rotary evaporate to dryness.

Gas-chromatographic determination

The residue derived is dissolved in 2 ml. ethanol hexane mixture and diluted to a suitable volume (V_{End}). An aliquot of this solution (V) is injected into the gas chromatograph.

Operating conditions

Gas chromatograph : With Nitrogen specific detector (NPD/TID)

Colum : Glass, 2 mm i.d. 1.5 m long; packed with 3 % CP Wax 40M on Gas Chrom Q,80-100 mesh (chrom-pack)

Column temperature : 245 °C

Injection port temperature : 250 °C

Temperature : 250 °C

Gas flow rates : Nitrogen carrier, 36 ml./min

Hydrogen 3 ml./min

Air 50 ml./min

Attenuation : 16

Recorder : 1 mV; chart speed 10 mm/min.

Injection volume : 2 µL

Retention time for propiconazole :2 min 20 s

Estimation of Triazole Fungicides:

Triazole pesticide / fungicide residues extracted from soil with acetone are filtered, evaporated to small quantities, diluted with water and saturated sodium chloride solution and partitioned into dichloromethane. The dichloromethane extracts are rotary evaporated to dryness and the residues are cleaned up by column chromatography on aluminium oxide. Triazoles are determined by gas chramatography using Nitrogen Phosphorus Detector (NPD).

Experimental:

(1) Apparatus

[1] Analytical balance with sensitivity of 0.1 mg, [2] Top loading balance with sensitivity of 1 mg.

[3] **Gas chromatograph with Gas Chromatographic column**: DB-5, megabore, 30 m long, 0.53 mm i.d. 0.5 µm film thickness (or) similar, [4] Nitrogen Phosphorus Detector (NPD),[5] Mixer grinder , [6] Laboratory mechanical shaker , [7] Conical flasks , [8] Volumetric flasks, [9] Buchner funnel , [10] Vacuum flask/filtration flask, [11] Separatory funnels[12] Filter paper, WhatmanNo.l, [13] Round bottomed flasks, [14] Rotary vacuum evaporator, [15] 40 °C bath temperature, [16] Chromatographic tubes, 18 mm × 450 mm, [17] Micro syringe, 10 µL.

Reagents:

[1] Reference standards of known purities of Hexaconazole, Propiconazole, Penconazole, Myclobutanil, Triademifon and Triadiminol , [2] Acetone, [3] Dichloromethane, [4] Toluene, [5] n-Hexane, [6] Sodium chloride, [7] Anhydrous sodium sulfate,

[8] **Aluminium oxide activity grade V**: The 100 g. Aluminium oxide neutral active is taken in a 300 ml. Erlenmeyer flask (with ground joint) and 15 ml of water is added drop wise with continuous swirling. Immediately the flask is stoppered with a ground glass stopper and shook vigorously until all lumps disappear. It is stored in a tightly stoppered container for at least 2 h. before use.

Standard solutions:

The stock solution is prepared by dissolving 0.01 g. reference pesticide standards in 100 ml. n-hexane (add acetone if required for solubilization). For GC determinations a mixed pesticide standard solution is prepared by taking suitable aliquots from the above solutions in to 100 ml. volumetric flask and diluting them with ethyl acetate.

Sample preparation:

Finely ground the soil samples are taken and mixed well in a mixer grinder.

Extraction:

The 50 g. of finely ground soil is weighed and transferred into 500 ml. conical flask followed by addition of 200 ml. acetone. The container shook for 2 h. on a mechanical shaker at slow to moderate speed. Then it is filtered under suction through a Whatman no. 1 filter paper placed on a Buchner funnel attached to a vacuum flask. The filter cake is washed with three more 25 ml. portions of acetone. The filtrate is pooled and washed into a 500 ml. round bottom flask. It is evaporated in rotary evaporator to about 50 ml. volume. The filtrate is transferred quantitatively into 1000 ml. separatory funnel followed by addition with 400 ml. double distilled water. The 50 ml. of saturated sodium chloride solution is also added in it. Then it is extracted three times with 100 ml. portions of redistilled dichloromethane. The dichloromethane phases is filtered through anhydrous sodium sulfate which is kept into a 1000 ml. round bottom flasks and evaporated in a rotary evaporator to near dryness.

Clean-up:

A cotton plug at the bottom of a chromatographic tube is placed. It is packed with 5.0 g. anhydrous sodium sulfate and 30.0 g. aluminium oxide of activity grade V. The 5.0 g. anhydrous sodium sulfate is also packed in tandem using n-hexane. The excess solvent is drained from the column until the level falls to the top of the packing. The extract from the above step is transferred quantitatively using three 5.0 ml. portions of dichloromethane: hexane (60: 40, v/v) solvent mixture ratio. It is eluted the column with 135 ml. of the same solvent mixture at a flow rate of approximately 2 drops per second. The elute is collected in a 250 ml. round bottom flask and evaporated in rotary evaporator to dryness.

Gas Chromatographic determination:

The residue derived from the above step is dissolved in ratio of acetone: hexane (2: 8. v/v) mixture. It isdiluted to suitable volume. The 1.0 µL of this solution is injected into GC equipped with Nitrogen Phosphorus Detector (NPD) operated under the following suggested parameters.

Column: DB-5, Megabore, 30 m long, 0.53 mm i.d., 0.5 µm film thickness
Injector temperature: 280°C
Detector temperature: 290°C
Column oven Initial Temperature (1): 200°C
Initial Hold Time: 10 min
Ramp rate: 15°C/min
Temperature (2): 225 °C
Hold time: 7 minute
Ramp rate: 15°C/min
Temperature (3): 280 °C
Final hold time: 5 minute
Carrier gas flow rate: 10 ml./min.
Makeup gas for detector: 30 ml./min.
Hydrogen flow rate: 3.5 ml./min.
Air flow rate: 110 ml./min.

Calculations:

$$Residue\ of\ each\ triazole\ \left(\frac{mg}{kg}\right) = \frac{As \times C \times D \times VI}{A_{std} \times W \times V2} \times f$$

Where,

As = Peak area of each triazole in sample.

A_{std} = Peak area of each triazole when standard injected.

C = Concentration of ppm of each triazole standard solution.

D = Sample dilution (ml.)

W = Weight of sample (g.)

VI & V2= Volumes of sample and standard injected.

$$f = Recovery\ factor = \frac{100}{Percent\ mean\ recovery}$$

Reference:

Indian Standard 34 (1272).

Fuel Analysis:

Fuels are the main energy sources for industry and domestic purposes.

"A fuel is a substance containing carbon as the major substituent which provides energy on combustion for industry and domestic purposes".

The combustion is the process of oxidation that provides heat energy. Every combustion is anoxidation but every oxidation is not combustion.

Ex: - Combustion of wood, Petrol and kerosene gives heat energy

Classification of Fuels:

Classification of fuels is based on two factors.

1. Occurrence (and preparation)
2. The state of aggregation

On the basis of occurrence, the fuels are further divided into two types.

(a) **Natural or primary fuels**: - These are found in nature such as Wood, peat, coal, petroleum, natural gas etc.

(b) **Artificial or secondary fuels**: - These are prepared artificially from the primary fuels.

Ex: - charcoal, coke, kerosene, diesel, petrol, coal gas, oil gas, producer gas, blast Furnace gas,etc.

The second classification is based upon their state of aggregation; the fuel can be divided into three types. Such as

a) **Solid fuels**: Ex. Wood, peat, lignite, dung, bituminous coal and anthracite coal (natural or primary fuels) ; Charcoal, coke etc. (Artificial or secondary fuels)
   Ex. Coal: It is Cheap, easy to store, less towards fire hazards, It is a slow combustion process, least Calorific value and least Heat efficiency.
b) **Liquid fuels**: Crude oil (natural or primary fuels); Petrol, diesel and various other fractions of petroleum (Artificial or secondary fuels).
   Ex. Crude oil: Costlier than solid fuels, Closed containers should be used for storing, more Risk towards fire hazards, Fast combustion process, high Calorific value, high Heat efficiency.
c) **Gaseous fuels**: Natural gas (natural or primary fuels); Coal gas, oil gas, bio gas, water gas etc. (Artificial or secondary fuels).
   Ex.Coal gas: It is costly than solid fuel, Storage space required is huge and should be leak proof, Very high towards fire hazards, since these fuels are highly inflammable, Very rapid combustion and efficient, Highest Calorific value, highest Heat efficiency.

Analysis of Coal:

The analysis of coal is helpful in its ranking.

The assessment of the quality of coal is carried out by these two types of analyses.

(a) Proximate analysis

(b) Ultimate analysis

(a) **Proximate analysis**: In this analysis, the percentage of carbon is indirectly determined. It is a quantitative analysis of the following parameters.

1. Moisture content
2. Volatile matter
3. Ash
4. Fixed carbon

1. **Moisture Content**: About 1 gram of finely powdered air-dried coal sample is weighed ina crucible. The crucible is placed inside an electric hot air-oven, maintained at 105 to

110^0C for one hour. The crucible is allowed to remain in oven for 1 hour and then taken out,cooled in desiccators and weighed. Loss in weight is reported as moisture.

$$Percentage\ of\ Moisture = \frac{Loss\ in\ weight}{Weight\ of\ coal\ taken} \times 100$$

2. **Volatile Matter:** The dried sample taken in a crucible in and then covered with a lid and placed in an electric furnace or muffle furnace, maintained at 925 + 2°C. The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then inside desiccators and weighed again. Loss in weight is reported as volatile matter on percentage-basis.

$$Percentage\ of\ volatile\ matter = \frac{Loss\ in\ weight}{Weight\ of\ coal\ taken} \times 100$$

3. **Ash:** The residual coal sample taken in a crucible and then heated without lid in a muffle furnace at 700 + 5°C for ½ hour. The crucible is then taken out, cooled first in air, then in desiccators and weighed. Heating, cooling and weighing are repeated, till a constant weight is obtained. The residue is reported as ash on percentage-basis.

$$Percentage\ of\ ash = \frac{Weight\ of\ ash\ left}{Weight\ of\ coal\ taken} \times 100$$

4. **Fixed carbon**: $Percentage\ of\ fixed\ carbon = 100 - \%\ of(Moisture + Volatile\ matter + Ash)$

Significance of proximate analysis: Proximate analysis provides following valuable information's in assessing the quality of coal.

1. **Moisture**: Moisture in coal evaporates during the burning of coal and it takes some of the liberated heat in the form of latent heat of evaporation. Therefore, moisture lowers the effective calorific value of coal. Moreover, it quenches the fire in the furnace.Hence, lesser the moisture contentbetters the quality of coal as a fuel. However, presence of moisture up to 10% produces a more uniform fuel-bed and less of "fly-ash".

2. **Volatile matter**: High volatile matter content means that a high proportion of fuel will distil over as gas or vapour, a large proportion of which escapes un-burnt. So, higher volatile content in coal is undesirable. A high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Hence, lesser the volatile matter, better the rank of the coal.

3. **Ash**: Ash is a useless non-combustible matter which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat thereby lowering the temperature.

Also, it often causes trouble during firing by forming clinkers which block the interspaces of the grate on which coal is being burnt. This in-turn causes obstruction to air supply; thereby the burning of coal becomes irregular. Hence, low the ash content is the indication of better the quality of coal. The presence of ash also increases transporting, handling and storage costs. It also involves additional cost in ash disposal. The presence of ash also causes early wear of furnace walls, burning of apparatus and feeding mechanism.

4. **Fixed carbon**: The high percentage of fixed carbon indicates greater is it's calorific and betters the quality coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. This also represents the quantity of carbon that can be burnt by a primary current of air drawn through the hot bed of a fuel. Hence, high percentage of fixed carbon is desirable. The percentage of fixed carbon helps in designing the furnace and the shape of the fire-box because it is the fixed carbon that burns in the solid state.

(b) **Ultimate analysis**: This is the elemental analysis and often called as qualitative analysis of coal. This analysis involves the determination of carbon and hydrogen, nitrogen, sulfur and oxygen.

1. **Carbon and Hydrogen**: About 1 to 2 g. of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO_2 and H_2O respectively. The gaseous products of combustion are absorbed respectively in KOH and $CaCl_2$ tubes of known weights. The increase in weights of these are then determined.

$$C + O_2 \rightarrow CO_2 \quad ; \quad 2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad ; \quad CaCl_2 + 7H_2O \rightarrow CaCl_2.7H_2O$$

$$Percentage\ of\ C = \frac{Increase\ in\ weight\ of\ KOH\ tube \times 12}{Weight\ of\ coal\ sample \times 44} \times 100$$

$$Percentage\ of\ H = \frac{Increase\ in\ weight\ of\ CaCl_2\ tube \times 2}{Weight\ of\ coal\ sample \times 18} \times 100$$

2. **Nitrogen**: About 1.0 g. of accurately weighed powdered coal is heated with concentrated H_2SO_4 along with K_2SO_4 (catalyst) in a long-necked Kjeldahl's flask. After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The unused acid is then determined by back titration with standard NaOH solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as follows:

$$N(\%) = \frac{Volume\ of\ acid \times Normality\ of\ acid \times 1.4}{Weight\ of\ coal\ taken}$$

3. **Sulfur**: Sulfur is determined from the washings obtained from the known mass of coal, used in bomb calorimeter for determination of a calorific value. During this determination, S is converted in to Sulfate. The washings are treated with Barium chloride solution, when Barium sulfate is precipitated. This precipitate is filtered, washed and heated to constant weight.

$$S(\%) = \frac{Weight\ of\ BaSO_4\ obtained \times 32}{Weight\ of\ coal\ sample\ taken\ in\ Bomb\ Calorimeter \times 233} \times 100$$

4. **Ash**: The residual coal taken in the crucible and then heated without lid in a muffle furnace at700 + 50°C for ½ hour. The crucible is then taken out, cooled first in air, then in desiccators andweighed. Hearing, cooling and weighing are repeated, till a constant weight is obtained.Theresidue is reported as ash on percentage-basis.

$$Ash(\%) = \frac{Weight\ of\ ash\ left}{Weight\ of\ coal\ taken} \times 100$$

5. **Oxygen**: It is determined indirectly by deducting the combined percentage of carbon, hydrogen, nitrogen, sulfur and ash from 100.

$$O(\%) = 100 - \%\ of\ (C + H + S + N + Ash)$$

Significance of ultimate analysis:

Carbon and Hydrogen: Greater the percentage of carbon and hydrogen better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile mater and hence, it affects the use to which the coal is put.

Nitrogen: Nitrogen has no calorific value and hence, its presence in coal is undesirable. Thus, a good quality coal should have very little Nitrogen content.

Sulfur: Sulfur although contributes to the heating value of coal, yet on combustion produces acids like SO_2, SO_3, which have harmful effects of corroding the equipment and also cause atmospheric pollution. Sulfur is, usually, present to the extent of 0.5 to 0.3% and derived from ores like iron, pyrites, gypsum, etc., mines along with the coal. Presence of sulfur is highly undesirable in coal to be used for making coke for iron industry. Since it is transferred to the iron metal and badly affects the quality and properties of steel. Moreover, oxides of sulfur pollute the atmosphere and leads to corrosion.

Ash: Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature.

Hence, lower the ash content better the quality of coal. The presence of ash also increases transporting, handling and storage costs. It also involves additional cost in ash disposal. The presence of ash also causes early wear of furnace walls, burning of apparatus and feeding mechanism.

Oxygen: Oxygen content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value, and low coking power. Moreover, oxygen is a combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one. An increase in 1% oxygen content decreases the calorific value by about1.7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen.

Liquid fuels:

Flash point: Flash point is the minimum temperature at which a liquid forms a vapor above its surface in sufficient concentration that it can be ignited. Flammable liquids have a flash point of less than 37.7^{o}C.

The flash point is a general indication of the flammability or combustibility of a liquid. The insufficient vapour is available to support combustion below the flash point. At some temperature above the flash point, the liquid will produce enough vapour to support combustion. (This temperature is known as the fire point.)

Ex. Gasoline has a flash point around -43^{o} C whereas diesel has flash points higher than 52^{o}C. Lower flash points are the indicators of good flammability and volatility. Therefore, gasoline makes faster vapour formation than diesel and instantly catches fire when spark occurred from an external flame source.

Aniline point: Aniline point is defined as the minimum temperature at which equal volumes of anhydrous aniline and oil mix together. Aniline being an aromatic compound freely mixes with aromatic. So a low aniline point indicates low diesel index (because of high percentage of aromatics).

Significance: High aniline point indicates that the fuel is highly paraffinic and hence has a high Diesel index and very good ignition quality. In case of aromatics the aniline point is low and the ignition quality is poor.

This test is useful for calculating Diesel Index.

Octane number: The knocking characteristic of a fuel can be easily expressed by octane number. The anti-knocking value of n-heptane is taken as 0 (zero) because n-heptane knocks very badly. Whereasthe anti-knock value of iso-octane is approximately taken as 100 because iso-octane knocks very little. Actually the octane number is the percentage of iso-octane in a mixture of n-heptane inorder to matches the knocking characteristics of the fuel. Ex. “80-octane” fuel is onewhich has the same combustion characteristics as an 80:20 mixture in iso-octane and n-heptanes.

Gasoline with octane rating as high as 135 are used for aviation purposes. The octane number ofpoor fuels can be raised by the addition of extremely poisonous materials as tetra ethylene lead$(C_2H_4)_4Pb$ and diethyl-telluride $(C_2H_4)_2Te$.

Octane rating: It has been found that n-heptaneknocks very badly and henceit’s anti-knockvalue has arbitrarily been given zero. On the other hand, isooctane (2: 2: 4 – trimethyl pentane) has very little knocking.So its anti-knock value has been given as ‘100’. Thus, octanenumber (or rating) of a gasoline (or any other internal combustion engine fuel) is the percentageof isooctane in a mixture of isooctane and n-heptane which matches the fuel under test in knocking characteristics.

Advantages: Usually petrol with low octane number is not good quality petrol. It often knocks(i.e., produces huge noise due to improper combustion). As a result of knocking the petrol is wasted as well as the energy produced cannot be used in a proper way. The

addition of tetra ethyl lead prevents knocking. Hence it saves money and energy. Usually 1.0 to 1.5 ml of TEL is added per 1(one) lit.of petrol.

Carbon residue: The carbon residue of a fuel is the tendency to form carbon deposits under high temperature conditions in an inert atmosphere, and may be expressed commonly as Micro Carbon Residue (MCR) or alternatively Conradson Carbon Residue (CCR). It should be noted that numerically MCR is effectively the same as CCR.

The overall relationship between actual diesel engine performance and carbon residue is poor.However, the carbon residue value is considered by some to give an indication of thecombustibility and carbonaceous deposit forming tendencies of a fuel.

The carbon residue provides information on the carbonaceous deposits which will result from combustion of the fuel. For fuels with a high carbon- high carbon/hydrogen ratio, it is proved more difficult to burn them fully which results in increased deposits in the combustion and exhaust spaces. Fuels with a high carbon residue value may cause problems in older engines when they are operating under part load conditions. The carbon residue value of a fuel depends on the refinery processes employed in its manufacture.

Gaseous fuel:

Producer gas: It is a mixture of combustible gases CO and H_2 with large quantities of non-combustible gases CO_2 and N_2

The average composition of producer gas is given below.

CO = 22- 30%, H_2 = 8 - 12 %, CO_2 = 3%, N_2 = 52 - 55 %

Its calorific value is 1300 Kcal /m^3.

Uses: It is used:

(i) In heating furnace in metallurgical operations. (ii) As a reducing agent.

Water Gas: It is a mixture of combustible gases CO and H_2 with a little quantity of non-combustible gases CO_2 and N_2.

The average composition of water gas is given below.

H_2= 51 %, CO = 14 %, CO_2 = 4%, N_2 = 4%,

Its calorific value is 2800 Kcal / m^3

Uses: It is used as: (i) An illuminating gas. (ii) A fuel. (iii) A source of H_2 Gas.

Calorific value: The calorific value of a fuel can be defined as “the total quantity of heat liberated when a unit mass of the fuel is completely burnt in air or oxygen”.

The prime property of a fuel is its capacity to supply heat. Fuels essentially consist of carbon,hydrogen, oxygen and some hydrocarbons. The heat that a particular fuel can give is due tothe oxidation of carbon and hydrogen. Normally when a combustible substance burns the totalheat depends upon the quantity of fuel burnt, its nature, air supplied for combustion and certainother conditions governing the combustion. Further the heat produced is different for differentfuels and is termed as its calorific value.

There are different units for measuring the quantity of heat. They are:

(a) Calorie (c) British thermal unit (B.Th.U)

(b) Kilocalorie (d) Centigrade heat unit (C.H.U)

(a) **Calorie**: It is the amount of heat required to increase the temperature of 1.0 gram of waterthrough one degree centigrade.

(b) **Kilocalorie**: This is the unit of heat in metric system and is defined as the quantity of heatrequired to raise the temperature of one kilogram of water through one degree centigrade.

(c) **British thermal unit (B.Th.U)**: This is the unit of heat in English system and is defined as"thequantity of heat required to increase the temperature of one pound of water through of onedegree of Fahrenheit.

1 B.Th.U = 252 cal = 0.252 k.cal

(c) **Centigrade heat unit (C.H.U)**: It is the quantity of heat required to raise the temperature of onepound of water through one degree centigrade.

1 k.cal = 3.968 B.Th.U = 2.2 C.H.U

Inter conversion of various units of heat:1 kg = 2.2 lb and $1^oC = 1.8\ ^oF$,

1 k.cal = 1000 cals = 3.968 B.Th.U = 2.2 C.H.U ;1 B.Th.U = 252 cals

Units of calorific value:

- ✓ For solid or liquid fuels: cal/g or k.cal/kg orB.Th.U/lb
- ✓ For gaseous fuels: k.cal/cubic meter or k.cal/m^3, B.Th.U/ft^3, or B.Th.U/cubic feet

Relation between various units:1 k.cal/kg = 1.8 B.Th.U/lb = 1 cal/g

1 k.cal/m^3= 0.1077 B.Th.U/ft^3; 1B.Th.U/ft^3 = 9.3 k.cal/m^3

Gross calorific value (GCV): It is the heat liberated when a unit quantity of fuel is completely burnt and theproducts of combustion are cooled to room temperature. This heat includes the latent heat ofcondensation of water. Because when a fuel containing

hydrogen is burnt, the hydrogen presentis converted to steam. As the products of combustion are cooled to room temperature, the steam gets condensed into water and the latent heat is evolved. Thus the latent heat of condensation ofsteam, so liberated, is included in the gross calorific value.

Higher calorific value (HCV) or gross calorific value is defined as the total amount of heatliberated, when unit mass or unit volume of the fuel has been burnt completely and the productsof combustion are cooled down to 15 ^{o}C.

Net calorific value or lower calorific value (LCV): lower calorific value is defined as "the netheat produced, when unit mass or unit volume of the fuel is burnt completely and the combustionproducts are allowed to escape.

Net calorific value is the gross calorific value excluding the latent heat of condensation of water(the weight of water formed is nine times the weight of hydrogen in the fuel).

Therefore,

LCV or NCV = HCV – Latent heat of water vapour formed

Net calorific value = Gross calorific value – (Mass of hydrogen per weight of fuel burnt × 9 ×latent heat of vaporization of water).

Latent heat of steam is 587 kcal/g.

Net calorific value = Gross calorific value – 52.83 × %H

Where % H = percentage of hydrogen.

The gross and net calorific values of coal can be calculated by **bomb calorimeter**.

$$GCV = 339 \times \%C + 1427\left(\%H - \frac{\%O}{8}\right) + 22 \times \%S \quad ; \ Moist\ basis\ (Dulong\ formula)$$

$$NCV = GCV - 24.44(9 \times \%H + \%M) \quad Moist\ basis\ ; \quad \%M = Percentage\ of\ moisture$$

$$NCV\ dry\ basis = NCV\ moist\ basis \times \frac{100}{(100 - \%M)}$$

Reference

1- Determination of total nitrogen in soil and plant : A. K. Upadhyay and Rakesh Sahu, Department of Soil Science and Agricultural Chemistry, College of Agriculture, J.N.K.V.V., Jabalpur

2- Determination of Phosphorous in Soil and Plant: R. K. Thakur, Department of Soil Science and Agricultural Chemistry, College of Agriculture, J.N.K.V.V., Jabalpur.

3- Bartlett, GN, Craze, B, Stone, MJ & Crouch, R (ed) 1994, Guidelines for Analytical Laboratory Safety. Department of Conservation & Land Management, Sydney.
4- Bray, RH & Kurtz, LT 1945, Determination of total, organic, and available forms of phosphorusin soils. Soil Science, 59: 39-45.
5- Menage, PMA &Pridmore, B 1973, Automated determination of phosphate using Bray No 1 Extractant.CSIRO Division of Soils. Notes on Soil Techniques, pp.80-82.
6- METHODS OF SOIL AND PLANT ANALYSIS
With Special Reference to Strontium 90 Contamination
W. R. HEAU, R. G. MENZEL, H. ROBERTS, JE., and M. H. FREEE, Soil and Water Conservation Research Division, Agricultural Research Service.
7- Manual of Pesticide Residues analysis Vol. II, (1992).P 281-286, edited by Hens Peter Their.
8- P. C. Jain, Monica Jain, "Engineering Chemistry", Dhanpat Rai Publishing Company, 15th Edition, 2015.
9- Shasi Chawla, "Text Book of Engineering Chemistry", Dhantpat Rai Publishing Company, New Delhi, 1 st Edition.

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