

### Experiment no. 3

**Aim:** Analysis / Identification of high explosives using chromatographic technique

[Analysis of picric acid by thin layer chromatography- TLC].

#### Requirements:

- a) Test Sample: Picric acid (synthesized in lab).
  - b) Materials: Beaker(s), capillary tube(s), conical flask (Erlenmeyer flask), glass rod, measuring cylinder, measuring scale, pencil, spatula, sprayer, TLC plate, TLC chamber, watch glass.
  - c) Instruments: Hot air oven, water bath, weighing balance, UV chamber
  - d) Chemicals: Benzene, concentrated sulphuric acid, concentrated nitric acid, diethyl ether, ethanol, petroleum ether, phenol, silica gel G, and standard picric acid (commercially available).
- Ice and distilled water.

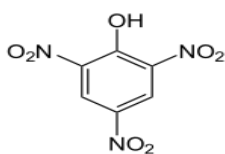
#### Theory:

High explosives are detonating explosives. Detonation is the explosion effect that is caused by the transmission of high speed shock wave when the explosive compound or mixture of compounds decomposes and liberates energy. The chemical reaction propagates with such rapidity that the rate of reaction zone into the material exceeds velocity of sound and is greater than 1000m/s. High explosives are further sub-divided in to two groups according to their susceptibility to initiation i.e. Primary explosives and Secondary explosives.

Here, the sample analysed is a secondary high explosive (generally used as the main charge):

#### Picric acid (2, 4, 6-trinitrophenol)

Phenol with concentrated sulphuric acid at high temperature doesn't form any interactive molecule. Hence, steric repulsion overcomes the attraction, thus at high temperature para phenol sulphonic acid is obtained. Para phenol sulphonic acid when reacts with concentrated nitric acid at high temperature due to prolonged heating, produces a mixture of ortho and para nitrophenol also termed as 2,4,6-trinitrophenol or picric acid.



Chemical structure:

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Properties of compound are: (On blank side)

|                      |                                  |
|----------------------|----------------------------------|
| Colour:              | yellow crystals                  |
| Solubility:          | soluble in water, ether, alcohol |
| Empirical formula:   | $C_6H_3N_3O_7$                   |
| Molecular weight:    | 229.1                            |
| Deflagration point:  | 3000°C                           |
| Impact sensitivity   | 0.75 kpm                         |
| Solidification point | 122.5°C                          |

### Thin layer chromatography

Thin layer chromatography, or TLC, is a method for analysing mixtures by separating the compounds in the mixture. After the sample has been applied on the plate, a solvent or solvent mixture (known as the mobile phase) is drawn up the plate via capillary action. Because different analytes ascend the TLC plate at different rates owing to affinity with stationary phase, separation is achieved. The  $R_f$  value (retardation factor) is used to quantify the movement of the materials along the plate.  $R_f$  is equal to the ratio of the distance travelled by the substance to the distance travelled by the solvent. Its value is always between zero and one. The  $R_f$  for a compound is a constant from one experiment to the next only if the chromatography conditions such as solvent system; adsorbent; thickness of the adsorbent; amount of material spotted and temperature are also constant.

### Procedure:

#### 1. Synthesis of picric acid

- In an Erlenmeyer flask, 2 ml phenol mixed with 3.5 ml concentrated sulphuric acid, dark solution observed.
- The flask containing the mixture was heated on a hot water bath at 80°C for 30 minutes.
- The heated solution kept in an ice bath at 0°C-5°C for cooling.
- On cooling, 12.5 ml concentrated nitric acid added drop-wise keeping flask in the ice bath while stirring constantly.
- The flask containing the formed solution was placed on a boiling hot water bath at 100°C for 1 hour until all the nitrogen dioxide gas goes off followed by cooling in the ice water bath.
- On cooling, 30 ml cold distilled water added (to precipitate picric acid).

- The solution was filtered using filter paper; thereby, collection of the crude picric acid.
- Recrystallization carried out to purify the product by addition of ethanol followed by heating till dissolution.
- Standby to let the crystal settle down and re-filtered.

Storage:

- Picric acid stored in dry, dark environment away from any potential source of ignition, or
- Alternatively stored in wet to reduce risk of explosion as it is vulnerable to shock and friction, or
- Stored in bottle under a layer of water in laboratories.

Precautions:-

1. Glassware's handled with care.
2. Caution in handling acids.
3. Holder / tongs usage for heated glassware's.
4. Prevention using mask against fumes inhalation as may be poisonous.

## 2. Thin layer Chromatography

**Table A (on blank side)**

| Sr. No | Mobile phase                   | Ratio  |
|--------|--------------------------------|--------|
| 1      | Petroleum ether: benzene       | 2:8    |
| 2      | Petroleum ether: acetone       | 7:3    |
| 3      | Petroleum ether: ethyl acetate | 8:2    |
| 4      | Water: methanol: acetonitrile  | 11:9:2 |
| 5      | Toluene: isopropanol           | 16:1   |
| 6      | Petroleum ether: diethyl ether | 6:4    |

### A. *Preparation and Activation of TLC plates*

- The glass TLC plates were cleaned with water and then air-dried.
- The silica gel slurry prepared by mixing a sufficient amount of silica gel-G with distilled water in the ratio of 2:1 while stirring slowly with a glass rod, till the desired consistency (with homogenous nature) obtained.

- The slurry poured onto the glass slide from one side and evenly spread to obtain uniform thickness. The plate were air dried.
- Before an hour or two of experiment, TLC plates were activated by placing in a thermostatically controlled oven at 110°C for a duration of 45 minutes.
- TLC plate were observed for non-uniformity or if any cracks develop owing to over activation, such plates if any were discarded.

**B. *Preparation of mobile phase***

- In TLC tank / TLC development chamber, 100 ml solvent system prepared by mixing in appropriate ratio (refer table A).
- Chamber covered with a lid and left to stand for at-least 30 minutes for the saturation of chamber such that equilibrium obtained before placing the TLC plate for development.

**C. *Spotting of sample***

- Spotting was done using a capillary tube immersed into the sample solution such that liquid is drawn into the capillary.
- Very gently the end of the capillary tube pressed on the prepared TLC plate at a distance of 2 cm from the base.
- Carefully sample spotting done to avoid tailing of sample as well as contamination of the adjacent sample.
- The spot was air-dried and repeated spotting done directly over the original spot.
- Two spots done; one the synthesized sample and other, commercial standard.

**D. *TLC plate development***

- Before placing the TLC plate in the developing chamber, double checked the plates, such that the solvent level is below the sample spot. The sides of the plate did not touch the jar.
- The plate placed vertically in the developing jar with the top end leaning against the jar.
- The jar was sealed and allowed the solvent to run until 2-3 cm from the top of the plate.
- The plate was removed from the tank and marked immediately for the solvent front with a pencil. The plate was allowed to dry.

E. *Visualization of sample*

- The plate observed in UV chamber or sprayed with ethylene diamine to view the spots (refer table A).

**Observation and Calculation: (On blank side)**

| Sr. No. | Mobile Phase                   | Distance travelled by solute (x) |                                | Distance travelled by solvent (y) | Rf value = x/y |      | HR <sub>f</sub> = R <sub>f</sub> *100 |          |     |
|---------|--------------------------------|----------------------------------|--------------------------------|-----------------------------------|----------------|------|---------------------------------------|----------|-----|
|         |                                | Synthesized (test) sample (A)    | Commercial standard sample (B) |                                   | (A)            | (B)  | Ref                                   | Obtained |     |
|         |                                |                                  |                                |                                   |                |      |                                       | (A)      | (B) |
| 1       | Petroleum ether: benzene       | 1.1 cm                           | 0.4 cm                         | 5.9 cm                            | 0.18           | 0.06 | 41                                    | 18       | 6   |
| 2       | Petroleum ether: acetone       | 1.5 cm                           | 1.6 cm                         | 5.5 cm                            | 0.27           | 0.29 | 27                                    | 27       | 29  |
| 3       | Petroleum ether: ethyl acetate | --                               | --                             | 5.4 cm                            | --             | --   | 38                                    | --       | --  |
| 4       | Water: methanol: Acetonitrile  | 5.4 cm                           | 5.2 cm                         | 6.5 cm                            | 0.83           | 0.8  | 76                                    | 83       | 80  |
| 5       | Toluene: isopropanol           | 1.1 cm                           | 0.9 cm                         | 5.8 cm                            | 0.18           | 0.15 | 9                                     | 18       | 15  |
| 6       | Petroleum ether: diethyl ether | --                               | --                             | 5.2 cm                            | --             | --   | 33                                    | --       | --  |

**Inference:** On the basis of observation and calculations, it can be inferred that in: (on blank side)

|   | Mobile Phase             | Inference                                  | Possible reasons  |
|---|--------------------------|--|---|
| 1 | Petroleum ether: benzene | Rf - half the value compared to reference. | Low polarity solvents <sup>#</sup>                                  |
| 2 | Petroleum ether: acetone | Rf – Matches the reference value           | Low polar : mid polar (appropriate ratio and conditions maintained) |

|   |                                   |  |   |
|---|-----------------------------------|--|---|
| 3 | Petroleum ether:<br>ethyl acetate | Sample run did not took place.   | Chamber equilibrium may not be appropriate. Or<br>excess amount of sample spotted or<br>Sample concentration too low.                                 |
| 4 | Water: methanol:<br>Acetonitrile  | Rf - slight differ than reference<br>value towards higher. Almost<br>negligible. | High polarity solvents *<br>(appropriate ratio and conditions<br>maintained)  |
| 5 | Toluene:<br>isopropanol           | Rf - has twice the value of<br>reference.  |   |
| 6 | Petroleum ether:<br>diethyl ether | sample run did not took place  | Least polarity solvents #<br>Chamber equilibrium may not be<br>appropriate. Or<br>excess amount of sample spotted or<br>Sample concentration too low. |

Note:

# Low polarity solvents (petroleum ether) cause the spots to move more slowly i.e. If the solvent is of too low a polarity the components will not move enough, and again separation will not occur (Rf's will be too small).

\* High polarity solvents (water, isopropanol) cause the spots to move very fast i.e. If a development solvent of too high a polarity is used, all components in the mixture will move along with the solvent and no separation will be observed (Rf's will be too large).

Either extreme can cause poor separation.

### Conclusion:

Thus, it is concluded that secondary high explosives synthesized identified as picric acid.

Also, the efficient mobile phase for thin layer chromatography of picric acid are

Petroleum ether : acetone [7:3] and

Water : methanol : acetonitrile [11:9:2]