Examination of Chemicals in Trap Cases

(Phenolphthalein)

Introduction

- Although a number of different techniques using different chemicals such as fluorescent dyes, starch powder, phenolphthalein powders etc. have been adopted but phenolphthalein powder in anticorruption cases has remained most popular in India.

- Phenolphthalein is a weak acid; its unionized molecules are colorless while on ionization gives pink color.

- The sodium carbonate washings containing traces of transferred phenolphthalein from accused is submitted to Forensic Science Laboratories (FSLs) for examination.

- There are so many conventional and instrumental techniques (Thin Layer Chromatography, UV-Visible Spectrophotometer, High Performance Liquid Chromatography, High Performance Thin Layer Chromatography etc.) which may be used for the confirmation of phenolphthalein.

- Phenolphthalein is being used in most of the anticorruption cases.

- Phenolphthalein powder, a smooth white powder is generally applied in small quantity on the currency notes and other objects are likely to come in contact with hands, pockets etc. of the culprit resulting in its transfer (Locard’s principle of exchange).

(Locard’s Principle of Exchange: Wherever he steps, whatever he touches, whatever he leaves, even unconsciously, will serve as a silent witness against him. Not only his fingerprints or his footprints, but his hair, the fibers from his clothes, the glass he breaks, the tool mark he leaves, the paint he scratches, the blood or semen he deposits or collects. All of these and more, bear mute witness against him. This is evidence that does not forget. It is not confused by the excitement of the moment. It is not absent because human witnesses are. It is factual evidence. Physical evidence cannot be wrong, it cannot perjure itself, it cannot be wholly absent. Only human failure to find it, study and understand it, can diminish its value.)

- The objects (hand, bag, pocket etc.) are washed with a colorless solution of sodium carbonate (or sometimes with lime water), which becomes immediately pink confirming the touching of currency notes/ transferred of phenolphthalein to the object.

- Pink to deep red color is developed depending upon the quantity of phenolphthalein involved.
These washings are being collected and sent to the forensic laboratories along with other relevant materials for analysis.

**Introduction to Phenolphthalein:**

**Name:** Phenolphthalein

**Formula:** C\textsubscript{20}H\textsubscript{14}O\textsubscript{4}

**Short Names:** Often written as "HIn" or "phph"

**Synonym:** 3,3-Bis(4-Hydroxyphenyl)-1(3H)-Isobenzofuranone; 3,3-Bis(p-Hydroxyphenyl)Phthalide; Alpha-Di(p-Hydroxyphenyl)phthalide

**Appearance:** Pale Yellow.

**Effects:** It may cause eye and skin irritation. It may cause respiratory and digestive tract irritation.

**Target Organs:** Kidneys.

**Potential Health Effects**

**Eye:** May cause eye irritation.

**Skin:** May cause skin irritation.

**Ingestion:** Causes gastrointestinal irritation with nausea, vomiting and diarrhea.

**Inhalation:** May cause respiratory tract irritation.

**Chronic:** May cause kidney injury.

**Chemistry of Phenolphthalein**

- Phenolphthalein is a weak acid and is almost unionized.
- Its unionized molecules are colorless which on ionization give colorless H\textsuperscript{+} and pink colored phenolphthalein ions.
- In the presence of acid due to increase in the concentration of common ions (H\textsuperscript{+}), the dissociation of phenolphthalein is suppressed and thus the solution becomes colorless.
- While the addition of strong bases (e.g. KOH, NaOH) produces OH\textsuperscript{-} ions combine with the H\textsuperscript{+} ions from the phenolphthalein to form the ionized water.
- Thus more phenolphthalein ions are produced giving the pink color solution.
• **General method of extraction of phenolphthalein from hand wash:**

  Take appropriate amount of hand wash in a 100 ml beaker. Acidify this solution with dilute hydrochloric acid (till acidic to congo red), extract the solution with 3x30 ml diethyl ether. The extracted residue was crystallized with hot water as white crystalline mass (M.P. 213°C). Concentrate the ether extract and use for further analysis.

**Materials and methodology**

**THIN LAYER CHROMATOGRAPHY:**

- The ether extract as above, was studied by Thin Layer Chromatography (TLC) using silica gel plates.
- Standard phenolphthalein was used for comparing.
• The plate was developed in a suitable solvent system and then sprayed with the suitable spraying reagent given below.

• TLC plate was exposed to ammonia vapor for visual development of un-decomposed phenolphthalein as pink spot.

• It was reported that ammonia as spray reagent for the detection of phenolphthalein is neither sensitive enough to detect the traces nor the pink spot developed by it is stable and hence is unsuitable for routine analysis in Forensic Science Laboratories.

• Alternatively all the spots should be visualized by iodine fumes, treatment of the developed plate and comparison with the standards is done.

**Mobile Phase:**

- Benzene: Dioxane: Acetic acid (75: 15: 10)
- Chloroform: Acetone (4:1)
- Ethyl acetate: Methanol: Ammonia (80:10:5)

**Stationary phase:** Silica Gel G

**Visualizing reagent:**

- UV light
- Exposed to ammonia vapor
- Spray with neutral ferric chloride solution.
- Iodine fumes
- With 1 % solution of potassium permanganate in 0.25 M sulfuric acid.
- Diazocoupling reagent – prepared by mixing 25 ml of p-nitroaniline solution (0.3 % w/v) in hydrochloric acid (8%w/v) with 1.5 ml of a 5 % w/v solution of sodium nitrite in water followed by 10 % w/v of sodium hydroxide solution in water.

**UV-SPECTROSCOPY:**

- Take UV spectra of this compound in aldehyde free alcohol gives absorbance maxima at 225 and 285 nm.
- A normal UV spectrum of phenolphthalein is known to show maxima at 277 nm in methanol.
- It was found that the first and second derivative UV- spectra of the ethanolic solution is more informative and is more specific.
**Troubleshooting in Trap Cases**

- Phenolphthalein is known to give pink color in alkaline at a concentration as low as $0.005 \times 10^{-3}\%$ (5µg per 100ml).

- The pink color of this solution persists for some days to some months depending upon the quantity of phenolphthalein and the strength of alkali solution.

- It gradually fades and sometimes becomes colorless at the time of trial in the court.

- The fading of color solution may be due to two reasons:
  - pH of the solution is out of limits (pH = 8.2)
  - Phenolphthalein has been broken into other colorless products.

- In the first case color can be regenerated by adjusting pH of the solution.

- In the second case, this phenomenon can be explained on the scientific basis of that the color of phenolphthalein fades due to its breaking down into 2 (4-hydroxybenzoyl) benzoic acid and phenol in alkali medium. The chemical break down of the alkaline phenolphthalein is caused by the oxygen present in the air. This can be prevented by the addition of hydroquinone which is strong antioxidant combines with the oxygen more rapidly than alkaline phenolphthalein does and thus retards the above reaction. It can be easily mixed with phenolphthalein powder before dusting the currency notes.

- The presence of hydroquinone will provide another parameter to prove the transfer of money especially in those cases when the plea is taken by the culprit that he uses phenolphthalein tablets as laxative. The presence of hydroquinone can be easily established on the basis of chemical and instrumental methods.

- Thus phenolphthalein used in trap cases is replaced by mixture of phenolphthalein and hydroquinone (100:2), the resulting pink color does not fade appreciably after 4 years and can be seen by naked eye. Hydroquinone is a colorless powder and does not give pink color in alkaline medium.

![Chemical Reaction Diagram]
Conclusion and Future Prospectus

- The colored alkaline phenolphthalein solution unfortunately has a tendency to fade away with passage of time due to chemical changes.

- If the initial solution is highly colored, with passage of time varying up to several months, its intensity may decrease but still it will be patently visible.

- On the other hand, if the alkali solution of phenolphthalein was only pink to light pink initially, because of very low quantity of transferred chemical it may become faint or even colorless after several weeks to months.

- Consequently when this physical evidence is finally produced in the court, often several months to year or more after the initial trap, the alkali solution may appear to be colorless or almost colorless.

- As the courts place reliance on the visual appearance of red color of the alkali solution of phenolphthalein as a proof of transfer of phenolphthalein.

- The absence or doubtful presence of phenolphthalein complicates matters.

- Defense often tries to take advantage of this situation.

- Although this problem has been solved by adding small quantity of hydroquinone (an antioxidant), but still more work has to be done in this area.