



VIDYASAGAR UNIVERSITY

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(BOT 403A) : Molecular Systematics

5. Adulteration of medicinal herbs



Course Coordinator

Prof. A.K.Mondal, FLS, FIAAT

Professor of Botany & Coordinator

UGC-DRS-SAP-II and DBT-BOOST-WB

Plant Taxonomy, Biosystematics and Molecular Systematics Laboratory

UGC-DRS-SAP-II and DBT-BOOST Supported Department

Department of Botany & Forestry

Vidyasagar University

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Adulteration of medicinal Herbs



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Definition

Adulteration is practice of substituting original crude drug partially or whole with other similar looking substances but the latter is either free or inferior in chemical and therapeutic properties.

OR

Adulteration in simple words is the debasement of an article.

OR

Adulteration is broadly defined as admixture or substitution of original or genuine article/drug with inferior, defective or otherwise useless or harmful substances.

Introduction

- ✓ The adulteration and substitution of herbal drugs is the burning problem in herbal industry and it has caused a major effect in the commercial use of natural products. Adulteration in market samples is one of the greatest drawbacks in promotion of herbal products.
- ✓ Adulteration it is a practice of substituting the original crude drug partially or fully with other substances which is either free from or inferior in therapeutic and chemical properties or addition of low grade or spoiled drugs or entirely different drug similar to that of original drug substituted with an intention of enhancement of profits.
- ✓ *An adulteration means a process of addition of impure, cheap and filthy substances to genuine drug in order to get more profits . The adulterants may not have pharmacological or therapeutic properties.*

Adulterant

The adulterant must be some material which is both cheap and available in fairly large amounts.

REASONS FOR ADULTERATION

1. Scarcity of the drug.
2. The high price of the drug in the market e.g: Clove, Cinnamon, Cardamom
3. It is very common with the contraband drugs e.g. Opium

Types of Adulteration Or Substitution of Herbal Drugs

- Different methods used for adulteration may be grouped as follows:

1. Substitution with Inferior Commercial Varieties

Due to morphological resemblance to the authentic drugs, different inferior commercial varieties are used as adulterant which may or may not have any chemical or therapeutic potential as that original natural drug

- E.g. Arabian Senna (*Cassia angustifolia*) and dog Senna (*Cassia obovata*) have been used to adulterate Senna (*Cassia senna*)
- E.g. Japanese ginger (*Zingiber mioga*) to adulterate medicinal ginger (*Zingiber officinale*).

2. Adulteration by Artificially Manufactured Substitutes

To provide the general form and appearance of various drugs, some materials are artificially manufactured and are used as substitute of the original one. E.g. artificial invert sugar for honey; paraffin wax after yellow coloration substituted for bees wax.

3. Substitution by Exhausted Drugs

Here the same plant material is mixed which is having no active medicinal components as they have already been extracted out. This practice is most common in case of volatile oil containing materials like clove, fennel etc.,

- where the dried exhausted material resembles the same like original drug (similarly with drugs like *Cascara sagrada* and ginger). Sometimes when coloring matters have been extracted or removed during exhaustion, the residue is re-colored with artificial dyes as is done with saffron and red rose petals.

4. Substitution by Superficially Similar but Cheaper Natural Substances

Usually here the adulterated product has no relation with the genuine article, may or may not have any therapeutic or chemical component desired,

- e.g. leaves of species - *Ailanthus* are substituted for belladonna, senna, mint etc.;
Leaves of *Phytolacca* and *Scopolia* for belladonna; Leaves of *Xanthium* for *stramonium* and dandelion for henbane;
Indian dill with European dill or caraway etc.

5. Adulteration by Addition of Worthless Heavy Materials

A large mass of stone mixed with Liquorice root, pieces of limestone are found in asafoetida and lead shot has occurred in pieces of opium etc.

6. Addition of Synthetic Principles

Sometimes to fortify inferior natural products, synthetic principles are added e.g. adding citral to oil of lemon; benzyl benzoate to balsam of Peru etc.

7. Usage of Vegetative Matter from the Same Plant

This is done by mixing adventitious matters or naturally occurring with the drug in excessive amount or parts of plant other than that which constitutes the drugs.

- For example liver warts and epiphytes growing in bark portion are mixed with Cascara or Cinchona; stems of buchu are sometimes cut into short lengths and added to the drug.
- Several factors are to be considered for the detrimental effects on the stored products.

Methods of Adulteration

- * Inferiority
- * Spoilage
- * Deterioration
- * Admixture
- * Sophistication
- * Superficially similar Inferior drugs
- * Artificially Manufactured substance
- * Using of Synthetic Drugs
- * Harmful Adulterants

1. Inferiority.

- * Replacement with substandard drug. Natural substandard condition, where a crop is taken whose natural constituents is below the minimum standard for that particular drug.
- * Adulterants resembles the original crude drug morphologically, chemically, therapeutically but are substandard in nature and cheaper in cost.
- * **Examples:**
 - * *Strychnos nux-vomica* adulterated with *Strychnos potatorum*,
 - * Indian senna adulterated with Arabian-senna,
 - * *Zingiber officinalis* adulterated with Japanese ginger,
 - * *Solanum xanthocarpum* adulterated with *Solanum mammosum*.
- * It can be avoided by more careful selection of plant material,



Strychnos nux-vomica



Strychnos potatorum



Indian senna



Arabian senna



Zingiber officinalis



Japanese Ginger



Solanum xanthocarpum



Solanum mammosum

2.Spoilage (Attack of Microbes).

- * Sub-standard condition produced by microbial or other pest infestation which makes a drug unfit for medicinal preparation.
- * **Examples:** Ativisha, Vatsanabha and Vacha. It can be avoided by giving more careful attention to the drying & storage conditions.



Spoilage (Attack of Microbes) in Herbal drugs

3.Deterioration.

- * Deliberate extraction of the constituents & the sale of the residue as the original drugs.
- * Refer to any impairment of the quality or value of a drug due to destruction or abstraction of valuable constituents by some physical processes.
- * Same drug is admixed but that drug is devoid of medicinally active substance as it has been already extracted.
- * Mainly volatile oil containing drugs like Fennel, Clove, and Coriander are adulterated by this method.



4. Admixture.

- * Refers to addition of one article to another through accident, ignorance or carelessness.
- * A part of same plant which is devoid of therapeutic action is mixed.
- * **Eg:** Stem portions are mixed along with leaf in drugs like –*Bala*; *Dhattura*;
- * Inclusion of soil and stone pieces in *Hingu*; *Sariba* root with adhering soil and other plants;
- * Clove is mixed along with leaves and petioles.

5. Artificially Manufactured Substances.

- * The drug is adulterated with substance which has been prepared artificially.

Examples: Properly cut, shaved Basswood – For nutmeg;

Yellow coloured paraffin wax for Bees wax.

6. Using of Synthetic Drugs.

- * Synthetic chemicals are used to enhance natural character.

Eg: Citral is added to citrus oils (like oil of lemon and oil of orange).

7.Sophistication.

- * Means addition of spurious or inferior material to an article with an intent to defraud.
- * The drugs which are in the form of powders are frequently adulterated by this method.
- * Example: Addition of wheat flour to powdered ginger, with enough capsicum to restore the pungency & curcuma to maintain the colour;
- * Powdered bark adulterated with brick powder.



8. Superficially Similar but Inferior Drugs.

* Inferior drugs may or may not have any chemical or therapeutic value.

Eg: Piper nigrum adulterated with Carica papaya;

* Bee wax adulterated with Japan wax;

* Belladonna leaves adulterated with Ailanthus leaves.

* Crocus sativus adulterated with Carthamus tinctorius;



9. Harmful Adulterants:

* Sometimes waste from the market are collected and admixed with the authentic drug.

Eg:

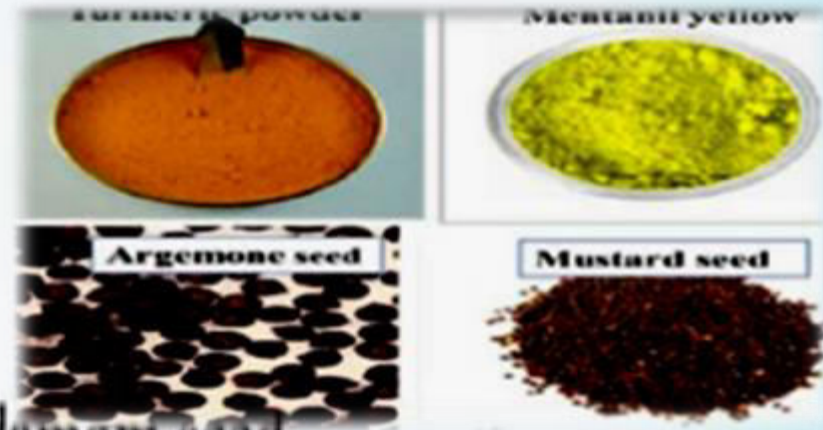
* Limestone in Asafoetida,

* Mentanil Yellow in Turmeric powder,

* Lead shot in Opium,

* Addition of rodent faecal matter in Cardamom seed,

* Argemone seed in Mustard seed, White oil in coconut oil.



Reasons for Adulteration

- * Confusion in vernacular names.
- * Lack of knowledge about authentic sources.
- * Similarity in Morphology.
- * Lack of authentic plants.
- * Unscientific collection.
- * High price of the drug in the market.
- * With the intention of enhancing profits.

TYPES OF ADULTERATION

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graph TD; A[TYPES OF ADULTERATION] --> B[1. Deliberate or Direct (Intentional) Adulteration]; A --> C[2. Accidental (In-deliberate) or Indirect adulteration];
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1. Deliberate or Direct
(Intentional)
Adulteration

2. Accidental
(In-deliberate) or
Indirect
adulteration

Deliberate adulteration: Are normally commercial mainly with the intention of enhancement of profits.

1. Direct or intentional adulteration.

- * Direct or intentional adulteration is done intentionally which usually includes practices in which an herbal drug is substituted partially or fully with other inferior products.
- * Due to morphological resemblance to the authentic herb, many different inferior commercial varieties are used as adulterants. These may or may not have any chemical or therapeutic potential.
- * This practice is most common in the case of volatile oil-containing materials, where the dried exhausted material resembles the original drug but is free of the essential oils.
- * Foreign matter such as other parts of the same plant with no active ingredients, sand and stones, manufactured artifacts, and synthetic inferior principles are used as substitutes.

A. Substitution with inferior quality.

Ideal properties of substituent

- * It shows similar morphology with crude drug.
- * It should cheaply available.
- * Non toxic in nature.
- * Compatible with crude drug.

| DRUG | ADULTERANT |
|----------------------|---------------------------------------------|
| Indian senna | Arabian senna , dog senna |
| Gentian | Picrorrhea , curroa |
| Tragacanth | Hog Tragacanth |
| Trichunous nuxvomica | Trichunous nuxblenda, strichunous nuxblenda |

B. Substitution with exhausted crude drugs

* Many drugs are extracted in large scale for the isolation of active constituent. Extraction process may doesn't change morphology of drug. And the extracted drug is called exhausted drug. There is a chance to adulterate crude genuine drug with it.

| DRUG | ADULTERANT |
|----------------|---------------------|
| Clove oil | With clove stem oil |
| Coriander | Oil from fruits |
| Cinnamon | Oil from leaves |
| Peppermint oil | Commint oil |

C. Substitution with similar morphology.

* In this type drugs are adulterated with similar morphology containing drugs;

| DRUG | ADULTERANT |
|----------------|--------------------------------------|
| Saffron | Dried flowers of carthamus tinctoris |
| Myrrh | Sented bedilum |
| Clove | Clove stocks |
| Tragacanth gum | Streculia gum |
| Stromonium | Leaves of xanthium |
| Bees wax | Japanese wax |

D. Substitution with artificially manufactured substances

*Some artificial agents are manufactured to get adulteration with crude drugs.

| DRUG | ADULTERANT |
|----------------|-----------------------------|
| Bees wax | Yellow paraffin |
| Honey | Invert sugar |
| Balsum of Peru | Addition of benzyl benzoate |

E. Substitution with harmful substances

❖ In this method defective and harmful substances are admixed with unorganized drugs

| DRUG | ADULTERANT |
|--------------|----------------|
| Opium | Lead shots |
| Coconut oil | White oil |
| Cocoa butter | 18 paraffin |

F. Substitution of powders

* Powdered varieties of crude drugs may be adulterated with the below

| DRUG | ADULTERANTS |
|---------------|------------------|
| Capsicum | Red sandals wood |
| Cinnamon | Hazel nut shells |
| Ipecac | Dextrin |
| Ginger powder | Exhausted ginger |

G. Substitution with foreign & fictitious materials

❖ Some times foreign matter is added to crude drugs;

| DRUG | ADULTERANTS |
|------------------|---------------------------|
| Myrrh | Quartz & mineral material |
| Resins | Colophony |
| Black pepper | Seeds of papaya |
| Nuxvomica powder | 19 Olive stone powder |

2. Indirect or unintentional adulteration.

- * Unintentional or undeliberately adulteration which sometimes occurs without bad intention of the manufacturer or supplier. Sometimes in the absence of proper means of evaluation, an authentic drug partially or fully devoid of the active ingredients may enter the market.
- * Factors such as geographical sources, growing conditions, processing, and storage are all factors that influence the quality of the drug.

I. Faulty collection of crude drugs.

- * Certain drugs are collected in specific season only, if not then the conc. Of chemical constituents may be vary;

| DRUG | COLLECTION SEASON |
|--------------------|-------------------|
| Wild cherry bark | autumn |
| Male fern | Late autumn |
| Solanaceous leaves | Summer |
| Cinnamon bark | 20 Rainy season |

*With this parameter we should remember that the stage of drug collection from plant;

| DRUG | STAGE WITH MAX.ACTIVITY |
|--------------------|--------------------------------|
| Linseed | When fully ripen |
| Coriander | When fully grown and ripen |
| Solanaceous leaves | Flowering stage |
| Belladonna root | At 3-4 years old |
| Opium capsules | Maturing stage |
| Wild cherry bark | Young stems |

II. Imperfect preparation.

- * While preparation of crude drugs it should be considered the step of collection which reflects the economical state.
- * Adulteration may takes place by collection of undesirable and inert part instead of desired part;

| DRUG | OFFICIAL PART | UNDESIRE PART |
|-----------|---------------------|-------------------|
| Ipecac | Roots & rhizomes | Arial stem |
| Fennel | fruit | Undeveloped fruit |
| Saffron | Style & stigma tops | Parts of corolla |
| Ginger | Rhizome | Curt |
| Pyrethrum | Flower heads | Steam & leaf |

III. Improper drying

* Faulty inadequate drying may cause adulteration;

| DRUG | FAULTY TREATMENT OF DRYING |
|-------------------|----------------------------------------------------------|
| Digitalis leaves | When leaves dried enzyme degrades the glycosides content |
| Corn of colchicum | Above 65°c temp, hydrolyses the drug |

IV. Improper storage and maintenance.

* Storage conditions also affect the quality of drug. Improper storage may leads to spoilage:

| DRUG | STORAGE CONDITION |
|---------------|-----------------------------------------|
| Volatile oil | In closed container stored in dark room |
| Cod liver oil | Stored in ambered colored bottles |
| Coffee | Avoid over heating |
| Ergot | Protected from moulds |

DISADVANTAGES OF ADULTRATION

- * Adulteration causes denaturation & degradation of product;
- * Adulteration may leads to deterioration of product;
- * Adulterants may completely destroy the active constituents;
- * May cause artificial scarcity of drug;
- * That leads to damage of dosage form;
- * Adulteration leads to altering of drug nature;
- * The adulterants may cause damage to patient;
- * Adulterants may cause death of patient;
- * They may cause un wanted side effects in patients;
- * They lead to increase price of product;
- * They cause to increase formulation price of dosage form;
- * Adulteration leads to damage of containers also.

Adulteration may be evaluated (or) measured by the following methods:

- ❖ Morphological or Organoleptic Test**
- ❖ Microscopic Evaluation**
- ❖ Chemical Evaluation**
- ❖ Physical Evaluation**
- ❖ Biological Evaluation**
- ❖ Analytical Methods**

1. Organoleptic evaluation or Morphological Evaluation

- * It means evaluation of drug by the organs of sense (skin, eye, tongue, nose and ear) or macroscopic evaluation and it includes evaluation of drugs by color, odor, taste, size, shape and special feature, like touch, texture etc. it is the technique of qualitative evaluation based on the study of morphological and sensory profile of whole drugs.
- * **eg.** The fractured surfaces in *cinchona*, *quillia* and *casacara barks* and *quassia* wood are important characteristics.
- * Aromatic odour of *umbelliferous fruits* and sweet taste of *liquorice* are the examples of this type of evaluation where odor of drug depends upon the type and quality of odourous principles (volatile oils) present.
- * Shape of drug may be cylindrical (*sarsapilla*), subcylindrical (*podophyllum*), conical (*aconite*), fusiform (*jalap*) etc, size represent length, breadth, thickness, diameter etc.

* color means external color which varies from white to brownish black are important diagnostic characters. The general appearance (external marking) of the weight of a crude drug often indicates whether it is likely to comply with prescribed standard like furrows(alternate depression or valleys), wrinkles (fine delicate furrows), annulations (transverse rings), fissures (splits), nodules (rounded outgrowth), scars (spot left after fall of leaves, stems or roots).

*Taste is specific type of sensation felt by epithelial layer of tongue. It may be acidic (sour), saline (salt like), saccharic (sweetish), bitter or tasteless (possessing no taste).

2. Microscopic Evaluation

- * It involves detailed examination of the drug and it can be used to identify the organized drugs by their known histological characters.
- * It is mostly used for qualitative evaluation of organized crude drugs in entire and powder forms with help of microscope
- * Using microscope detecting various cellular tissues, trichomes, stomata, starch granules, calcium oxalate crystals and aleurone grains are some of important parameters which play important role in identification of certain crude drug.
- * Crude drug can also be identified microscopically by cutting the thin TS (transverse section), LS (Longitudinal section) especially in case of wood and by staining them with proper staining reagents **e.g.** starch and hemicelluloses is identified by blue color with iodine solution, all lignified tissue give pink stain with phloroglucinol and HCl etc

* mucilage is stained pink with ruthenium red can be used to distinguish cellular structure. Microscopic evaluation also includes study of constituents in the powdered drug by the use of chemical reagents.

* Quantitative aspects of microscopy includes study of stomatal number and index, palisade ratio, vein-islet number, size of starch grains, length of fibers etc which play important role in the identification of drug.

3. Chemical Evaluation

- *Most of drugs have definite chemical constituents to which their biological or pharmacological activity is attributed. Qualitative chemical test are used to identify certain drug or to test their purity.
- *The isolation, purification, identification of active constituents is based on chemical methods of evaluation. Qualitative chemical test such as acid value, saponification value etc.

- *Some of these are useful in evaluation of resins (acid value, sulphated ash),
- *For *balsams* (acid value, saponification value and bester values),
- *For *volatile oils* (acetyl and ester values)
- *For *gums* (methoxy determination and volatile acidity).
- *Preliminary phytochemical screening is a part of chemical evaluation. These qualitative chemical tests are useful in identification of chemical constituents and detection of adulteration.

4. Physical Evaluation

- * Physical constants are sometimes taken into consideration to evaluate certain drugs.
- * These include *moisture content, specific gravity, optical rotation, refractive, melting point, viscosity* and *solubility* in different solvents.
- * All these physical properties are useful in identification and detection of constituents present in plant.

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5. Biological evaluation

- * Some drugs have specific biological and pharmacological activity which is utilized for their evaluation.
- * Actually this activity is due to specific type of constituents present in the plant extract.
- * For evaluation the experiments were carried out on both intact and isolated organs of living animals. With the help of bioassays (testing the drugs on living animals), strength of drug in its preparation can also be evaluated Some important biological evaluations are as follow:

I. Antibiotic activity

II. Ant fertility activity

III. Hypoglycemic activity

IV. Neuro-pharmacological activity

1. Antibiotic activity.

- * Some bacteria such as *Salmonella typhi*, *staphylococcus aureus* and *E. coli* are used to determine the antiseptic value (the degree of antiseptic activity e.g. phenol co-efficient of certain drugs).
- * The activity of antibiotics is also determined by using *Klebsiella pneumonia*, *Micrococcus flavus*, *Sarcira lutea* etc. living bacteria, yeast and molds are used to evaluate certain vitamins.
- * Microbiological assays by cylinder plate method and turbidimetric method are used in evaluation.

2. Antifertility activity.

- * Antifertility drugs include contraceptives and abortifacients. Contraceptive drugs are used to prevent pregnancy and abortifacient to terminate pregnancy.
- * Female rats are used for antifertility activity i.e. measure the pregnancy rate (antiovation and anti-implantation) and male rats are used for antispermatogenic activity (inhibition of spermatogenesis) and spermicidal activity (sperm motility) of herbal drugs.

3. Hypoglycemic activity.

- * Rabbits, rats or mice are used to test hypoglycemic activity of plant extract. Radio-immuno assay (RIA) or Enzyme linked immunosorbate assay (ELISA) are done for measurement of insulin levels.

4. Neuropharmacological activity.

- * Testing the herbal drugs with effects on central and autonomic nervous system. CNS acting drugs like cocaine (*Erythroxylum coca*), morphine (*Papaver somniferum*), cannabinal (*Cannabis sativa*) are tested using rodents.
- * For testing the herbal drugs for their effects on ANS **guinea pig ileum** for **antispasmodic activity**, **rabbit jejunum** for **adrenergic activity**, **rat phrenicnerve-diaphragm** for **muscle relaxant activity**, **frog rectus** for **skeletal muscles activity**.

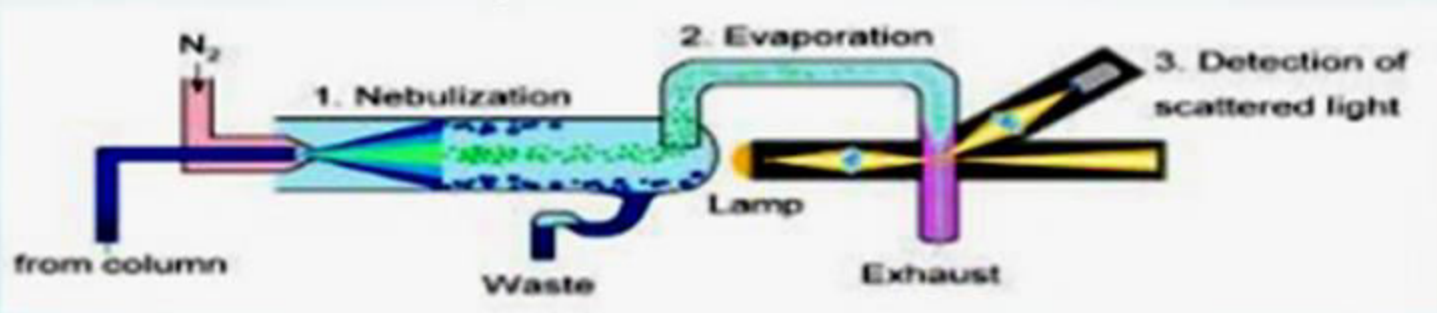
Analytical Methods: HPLC (High Performance Liquid Chromatography)

- * High performance liquid chromatography (HPLC), also known as high pressure liquid chromatography, is essentially a form of column chromatography in which the stationary phase consists of small particle (3-50 μ m) packing contained in a column with a small bore (2-5mm), one end of which is attached to a source of pressurized liquid eluent (mobile phase).
- * The three forms of high performance liquid chromatography most often used are *ion exchange*, *partition* and *adsorption*. HPLC is a popular method for the analysis of herbal medicines because it is easy to learn and use and is not limited by the volatility or stability of the sample compound.
- * In general, HPLC can be used to analyze almost all the compounds in the herbal medicines. Thus, over the past decades, HPLC has received the most extensive application in the analysis of herbal medicines.
- * Reversed-phase (RP) columns may be the most popular columns used in the analytical separation of herbal medicines. It is necessary to notice that the optimal separation condition for the HPLC involves many factors, such as the different compositions of the mobile phases, their pH adjustment, pump pressures³⁴, etc.

- * In order to obtain better separation, some new techniques have been recently developed in research field of liquid chromatography. These are micellar electrokinetic capillary chromatography (MECC), high-speed counter-current chromatography (HSCCC), low-pressure size-exclusion chromatography (SEC), reversed-phase ion-pairing HPLC (RP-IPC-HPLC), and strong anion-exchange HPLC (SAX-HPLC). They will provide new opportunities for good separation for some specific extracts of some herbal medicines.
- * On the other hand, the advantages of HPLC lie in its versatility for the analysis of the chemical compounds in herbal medicines, however, the commonly used detector in HPLC, say single wavelength UV detector, seems to be unable to fulfill the task, since lots of chemical compounds in herbal medicines are non-chromophoric compounds.
- * Consequently, a marked increase in the use of HPLC analysis coupled with evaporative light scattering detection (ELSD) in a recent decade demonstrated that ELSD is an excellent detection method for the analysis of non-chromophoric compounds

*This new detector provides a possibility for the direct HPLC analysis of many pharmacologically active components in herbal medicines, since the response of ELSD depends only on the size, shape, and number of eluate particles rather than the analysis structure and/or chromophore of analytes as UV detector do.

*Especially, this technique is quite suitable for the construction of the fingerprints of the herbal medicines. Moreover, the qualitative analysis or structure elucidation of the chemical components in herbal drug by simple HPLC is not possible, as they rely on the application of techniques using hyphenated HPLC, such as HPLC-IR, HPLC-MS, HPLC-NMR, for the analysis of herbal medicines.



Mechanism of ELSD detection



Acknowledgements:

I would like to thank our *Honourable Vice Chancellor* **Professor Ranjan Chakarborti** for giving me the opportunity to contribute in E-learning process which will be very much helpful for our students during unprecedented situation due to **CORONA Virus (COVID-19)**.

We shall overcome!!!!!!!

#SAVE FROM CORONA

Stay Home

Save your Life

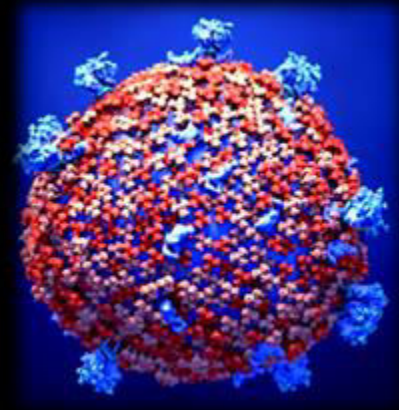
Save your Family

Save your Society

Save your Country

Save your beautiful Planet

THANK YOU





*Thank
you!*