A SEARCH OF REAGENTS FOR DETECTION AND IDENTIFICATION OF INSECTICIDES AND RELEVANT DRUGS OF FORENSIC INTEREST

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Abstract:

In the recent years in India, the use of different types of insecticides, fungicides, rodenticides and herbicides is increased in agriculture to protect the crops and commercial plants from insects to get good yield and also they are often used in houses to kill the mosquitoes, cockroaches, bed bugs and rats. Easy availability of these insecticides frequently misused in suicidal or homicidal poisoning. Analytical toxicology is an important branch of forensic Science. The number of fatal poisoning cases received for toxicological analysis is constantly increasing. The poison isolated from biological material in poisoning cases generally is in microgram quantities. For identification of these substances an attempt has been made to develop new technique by using Thin Layer Chromatography (TLC). These methods are highly sensitive and can be used for unequivocal identification of pesticides/drugs, etc. these method are discuss in this chapter. An attempt is being made to develop a new chromogenic reagent and analytical methods for selective detection of pesticides and drugs of forensic interest.

According to the WHO, about one million serious accidental cases and two million suicidal poisonings cases due to insecticides occurs worldwide every year, of which 200,000 patients die with most deaths occurring in developing countries. In India, organophosphorus, organochlorine, carbamate and pyrethroid are the commonest pesticides used and because of their easy availability, there is widespread abuse of these compounds with suicidal and homicidal intent.

In our study in Chapter II we have developed a new spray reagent for detection and identification of organophosphorous insecticide monocrotophos and dichlorvos. (An organophosphorous group has large application in the field of agriculture and is highly toxic for animal and human beings). A new chromogenic spray reagent for chromatographic detection & identification of monocrotophos is developed by thin layer chromatographic method. Monocrotophos on alkaline hydrolysis yields one molecule each of $O, O$-dimethyl phosphoric acid, and $N$-methyl acetoacetamide. The later reacts with vanillin to yield green color compound. This spray reagent is very useful for identification of monocrotophos in visceral material. The biological
impurities such as amino acids, peptides etc. present in visceral material do not interfere in the test.

In our study we developed another spray reagent for monocrotophos. The name of the reagent is benzil. Monocrotophos on alkaline hydrolysis yields dimethylphosphoric acid and N- methylacetoacetamide. The methylene group of N- methylacetoacetamide is located alpha to two carbonyl groups, which increases the reactivity of the two alpha hydrogen atoms. This active methyl group reacts with the chromogenic reagent benzil to give a pink colored compound. The thin layer chromatographic method developed in the present study, is very useful for quick and timely monitoring of monocrotophos from biological sample, which otherwise would have been time consuming, expensive and unsuitable for field use when sophisticated equipment employed.

In our study we have developed a new chromogenic spray reagent for chromatographic detection and identification of dichlorvos. A sensitive and selective thin layer chromatographic method for the detection and identification of dichlorvos using mercuric (II) chloride is described. The alkali hydrolysis product of dichlorvos reacts with mercuric (II) chloride to produce a black color spot. The reagent does not react with other organophosphorus, organochloro and carbamate insecticides and is specific for dichlorvos only. The constituents of viscera (amino acids, peptides, proteins etc) and plant materials do not interfere with the test.

Another newly developed group of insecticides is pyrethroid and neonicotinide.. For detection and identification of these insecticides in Chapter III we have developed a new chromogenic spray reagent for detection and identification of cypermethrin and imidacloprid. Pyrethroid insecticides containing hydrolysable cyanide moieties yields cyanide ions on alkaline hydrolysis. In the presence of p- benzoquinone reagent cyanide ions react to give a blue green fluorescence under UV light. These blue green fluorescence thus observed have Rf values 0.38, 0.42 and 0.46 for deltamethrin fenvalerate and cypermethrin respectively. The results obtained in this study lead us to conclude that the proposed method has detection limits, repeatability and recovery rates suitable for the detection of cypermethrin, fenvalerate and deltamethrin in biological materials.
In our study we also developed a new detection method for imidacloprid insecticide. A sensitive and selective thin layer chromatographic method for the detection and identification of imidacloprid insecticide using a new specific and chromogenic spray reagent \( p \)-dimethylaminobenzaldehyde is used. In acidic condition it reacts with imidacloprid insecticides to form a pink color compound. Other organophosphorous, organochloro, carbamates and pyrethroid insecticides do not interfere with the tests. The thin layer chromatographic method developed in the present study, is very useful for quick and timely monitoring of imidacloprid from biological sample, which otherwise would have been time consuming, expensive and unsuitable for field use when sophisticated equipment employed.

The increasing number of biological samples for poison detection, need versatile, sensitive and selective reagent. In our study in Chapter IV we have developed a new detection and identification method for endosulfan, carbaryl and nitrobenzene insecticide. In a search for a selective and sensitive reagent, potassium per magnate was found to be suitable for detection and identification of endosulfan in routine forensic toxicological analysis. Thin Layer Chromatography (TLC) is the method of choice because of its speed, low cost and versatility. A sensitive and selective thin layer chromatographic method is developed for the detection and identification of organochlorine insecticide endosulfan by using acidified potassium permanganate as a spray reagent. Endosulfan contains a cyclic Sulfite in its structure and is readily hydrolyzed by alkali to produce endosulfan glycol and sodium sulfite. The sodium sulfite produced in the reaction decolorizes the acidified potassium permanganate solution resulting in the two white spots thus obtained. The reagent is specific for endosulfan only. Other compounds for example organophosphorous, carbamate, and synthetic pyrethroid insecticides do not interfere with the test.

A sensitive and selective thin layer chromatographic method for the detection of carbamate insecticides, carbaryl, carbofuran and baygon is developed. The alkali hydrolysis product of carbamate insecticides reacts with FC reagent to produce a blue color compound. The reagent does not react with other organophosphorous, organochloro and carbamate insecticides and is specific for only carbamate insecticides which on hydrolysis give corresponding phenols. The constituent of
viscera (amino acid, peptides, proteins etc) and plant materials do not interfere with the test. The detection limit for carbaryl, carbofuran and baygon is about 0.2, 0.25 and 0.5 µg respectively. Again this method do not involve complicated extraction procedures or heating and consume less time. The current thin layer chromatographic methods use cheap chemicals and inexpensive equipment while providing good sensitivity. This makes the method highly suitable for quick and routine analyses of carbamate insecticides in biological materials.

Nitrobenzene is widely used insecticide in 10th century. For agriculture sectors now its 20 % & 40 % formulations are generally used. The acute oral toxicity to rats, (LD<sub>50</sub>) is 600 mg kg<sup>-1</sup>. In our study we also developed a new detection method for nitrobenzene. On reduction it gives aniline. Aniline in acidic condition reacts with furfural to form a colored Schiff base i.e. Dianyl of hydroxy glutaconic dialdehyde, which is cherry red in color. The reagent does not react with other organophosphorous, organochloro and carbamate insecticides and is specific for nitrobenzene insecticides. The results obtained in this study lead us to conclude that the proposed method has detection limits, repeatability and recovery rates suitable for the detection of nitrobenzene in biological materials.

There are so many problems for identification of these poisoning substances. There are no previous references for identification of such types of cases. By doing research and development work, and using the spray reagent developed by us, these cases are solved.

Thus the innovative methods applied by the author facilitated the identification of modern day insecticides and pesticides. This is the boost to forensic toxicology division to enhance the analytical methodologies by which the challenge of finding out modern day poisons can be achieved.