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Forensic Examination of Heroin and Its Cutting Agents

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Abstract

Heroin is a highly addictive drug synthesized from morphine. It can be injected, snorted, or smoked; it is most popular drugs in India. White heroin (diamorphine hydrochloride) is the purest form of the drug, but it's usually cut with other substances, significantly reducing its purity. The exhibits seized in the National Capital Territory of Delhi (NCT Delhi), forwarded to this laboratory were described as heroin/ smack/brown sugar. The exhibits were examined for its chemical constituents present in the contraband by using different analytical techniques viz. colour test, Thin Layer Chromatography used for qualitative analysis while Gas Chromatography Mass Spectrometry (GC-MS) used for quantitation and confirmation of the constituents present in the drugs. The exhibits received in different colour and texture which were found to contain diacetylmorphine (DAM), monoacetyl morphine, acetyl codeine and cutting agents such as caffeine, acetaminophen, phenobarbital, alprazolam and dextromethorphan. The 67 samples of contraband drugs were examined from the period of June 2018 to December 2018. The samples were found to contain minimum one and maximum five cutting agents. This study was helpful in establishing current trends in cutting agent compositional similarity in the different exhibits helpful in establishing chain of drug peddlers.

Keywords: Heroin, Caffeine, Phenobarbital, Acetaminophen, TLC, GC & GC-MS, Cutting Agents

Introduction

In order to successfully counter the ever-growing drug problem, there is an increasing need, to identify conspiracy links and trafficking routes and to gather background intelligence concerning both the number of sources of drugs and whether those sources are within a country or are "internationally" based and also the points of distribution and distribution networks. A scientific tool to complement routine law enforcement investigative work in this field is the characterization and impurity profiling and cutting agents of seized drugs. Drug characterization studies have shown that it is possible to link samples, to classify material from different seizures into groups of related samples and to identify the origin of samples. Such information can be used for evidential (judicial, court) purposes or it can be used as a source of intelligence to identify samples that may have a common origin or history. Drug characterization and impurity profiling may also assist in the identification of output from new illicit laboratories and in the monitoring of common methods used for drug manufacture, which, in turn, may provide information helpful to the maintenance of other intelligence gathering tools, for example, precursor-monitoring programmers. Finally, drug characterization and impurity profiling may also provide supporting evidence in cases where illicitly manufactured drugs need to be differentiated from those diverted from licit sources (UNODC) [1].

Heroin also called smack, junk, skag, dope, chaw and **brown sugar** (an adulterated form of Heroin), is a semi synthetic opioid derived from the morphine extracted from poppy plants (*Papaver somniferum*) to create a powder like material. Heroin is a banned drug as covered under Narcotic Drugs and Psychotropic Substances Act (NDPS Act-1985) [2] is easily available to drug addict. Heroin illicit an immediate and intense "high" (a euphoric feeling, or intense rush) that lasts only for a few minutes. Once the feeling passes, the user often wants nothing else except to feel that "high" again. A constant "need" for higher and higher doses comes next. And as the addict feeds his addiction in advanced quantities, often tolerance is developed. Suddenly, more and more of the drug is needed to receive a "quality high."

White heroin (diamorphine hydrochloride) is the purest form of the drug, but it's usually cut with other substances, significantly reducing its purity. Usually, street heroin is "cut" with other drugs or with substances such as caffeine, quinine, strychnine, phenobarbital, sugar, starch, powdered milk etc (Baconi, 2005) [3].

Heroin can be difficult to identify because it doesn't always appear to be white, but can actually appear pink, brown, beige, or off-white because of the different chemicals that may have been used to process it. Other substances, such as dextromethorphan, phenobarbital are cough suppressant and anticonvulsant medication that's even stronger compounds, are being used to cut heroin in certain markets.

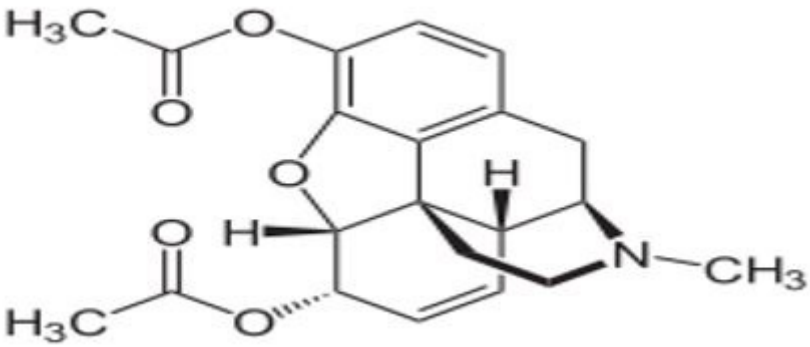


Figure 1: Structure of diacetylmorphine

Zhang et al. (2004) [4] have analyzed illicit heroin samples with GC-MS and its application in source of identification. Illicit heroin was found to contain O3&O6-acetylmorphiene, acetylcodiene, determined quantitatively adulterants such as acetaminophen caffeine and theophylline were detected qualitatively.

Chan et al. (2012) [5] developed gas chromatographic (GC) method validation for the analysis of major components in illicit heroin seized in Malaysia. GC method was developed to quantify various other cutting agents in addition to alkaloids, a simultaneous quantification of eight target analytes commonly found in illicit heroin within a 12 min run time.

Dams R et al. (2001) [6] conducted a study throughout ten years on impurity profiling of heroin samples. This study aims, for the identification and the quantification of minor components using physical and chemical toxicological analysis of seized samples, with special interest, impurities related to the origin and manufacturing.

Klemenc (2000) [7] has detected noscapine as an adulterant in illicit heroin samples. In this context, the appearance of illicit heroin samples characterized by a high noscapine content (up to 61%) and a high noscapine/whole morphine ratio (up to 3.5) is highlighted. All samples in this study (132) were seized in Slovenia, from 1997 to 1999 and were analyzed and confirmed by gas chromatography-mass spectrometry.

Schneider S, & Meys F (2011) [8] were Analyzed of illicit cocaine and heroin samples seized in Luxembourg from 2005-2010. In this study adulterants of 471 illicit cocaine and 962 illicit heroin samples seized in Luxembourg. In the seized cocaine samples, 14 different adulterants have been detected in which phenacetin and anthelminthic drug levamisole were found most abundant in the samples. Paracetamol and caffeine were the most abundant adulterants detected in heroin samples.

Brenneisen R, Hasler F (2002) [9], pyrolysis products from diacetylmorphine and adulterants of street heroin samples using GC-MS. The samples of heroin were smoked in laboratory condition on aluminum foil at 250-400^{0}C vapours collected in a condenser trap. A total of 72 pyrolysis products of diacetylmorphine, street heroin, and residues from aluminium foils used to smoke street heroin, typical by-products, and adulterants were detected by gas chromatography-mass spectrometry (GC-MS). The compounds identified typical street heroin constituents, like morphine, codeine, acetyl codeine, papaverine, and caffeine, are rather heat-stable. Other compounds, like noscapine and paracetamol, are pyrolyzed to a greater extent.

Zhang JX, Chen CY (2012) [10], has developed a rapid method for profiling samples of illicit heroin, if concerned with the derivatization and gas chromatographic separation followed by a fully automated data analysis. In this study six major constituents i.e., acetyl codeine, 6-monoacetylmorphine, papaverine, noscapine, codeine, and morphine were tested and analyzed and proved to be efficient and reliable providing information on links between illicit heroin samples.

O Neil PJ, Pitts JE (1992) [11] studied some physical and chemical features indicative of their origin of illicitly imported heroin products during 1984 to 1989. The samples from seizures of imported illicit heroin preparations of known geographical origin were examined. The typology developed in two previous surveys of illicit heroin products is applicable to many of the samples studied in this work, although significant changes have occurred in the chemical profile of illicit heroin products from certain geographical regions. Machata G, Vycudilik. (1980) [12], analyzed illicit heroin samples by gas chromatographic method. Morphine and 6-acetylmorphine in illicit heroin samples were determined by propionylation in aqueous solution. Heroin, 3-propionylmorphine and 6-acetyl-3-propionylmorphine are separated on methyl-phenylpolysiloxane liquid phases (5% phenyl content). The analytical procedure and the corresponding statistical data are presented together with the retention indices of typical street heroin concomitant drugs.

Esseiva P et al. (2003) [13] devised a methodology for illicit heroin seizures comparison in a drug intelligence perspective using large databases. To establish links between different illicit drugs chemical profiles, various distance or correlation measurements are presented. Different comparison methods have been tested and a method based on a correlation coefficient using a square cosine function was chosen to compare heroin chemical profiles.

Kaa E (1994) [14] has studied changing in impurities, adulterants and diluents of illicit heroin, during a 12-year period. 383 samples of illicit heroin seized in the western part of Denmark during the 12-year period 1981 to 1992. The purity of heroin varies from 45% in wholesale and 36% n retail samples. It was also found that SW Asian type heroin contains high concentration of noscapine, predominated from the mid-eighties. Heroin accounted for approximately half of the samples during the eighties, in recent years the base form has become predominant. During the early eighties caffeine and procaine were found frequently as additives next to sugars. From the middle and late eighties an increasing number of heroin samples were adulterated with phenobarbital and methaqualone. From the nineties the occurrence of phenobarbital and methaqualone has decreased, whereas paracetamol in combination with caffeine has become predominant.

Broseus J et al. (2016) [15], have critical reviewed the cutting of cocaine and heroin. Illicit drug cutting agents helpful in the solving of complex problem that requires the sharing of knowledge from addiction studies, toxicology, criminology and criminalistics. In this study deciphering the different aspects of cutting agents and their evolution in time and space and the analytical methodology implemented by forensic laboratories. The constituent's caffeine, diltiazem, hydroxyzine, levamisole, lidocaine and phenacetin are frequently detected in cocaine specimens, while paracetamol and caffeine are almost exclusively identified in heroin specimens.

Pichini S. et al. (2017) [16] have analyzed for purity and adulterants some recent drug seizures in Italy The data collected in this study describe an initial attempt to systematically introduce the qualitative and quantitative analysis of adulterants present in seized street drugs in Italy with the aim of improving surveillance and data sharing and for this purpose, the implementation of validated and standardized procedures are essential.

A comparative analysis of illicit heroin samples was carried out by Chiarotti M et al. (1991) [17]. The comparative analysis of street heroin samples a wide range of analytical techniques is necessary to obtain a valid amount of information about the sample composition. In the analytical sequence based on analysis of volatile compounds, opiates, diluents, adulterants and metals, by head space gas chromatography (GC-HS), gas chromatography mass spectrometry (GC-MS), thin layer chromatography (TLC), high pressure liquid chromatography (HPLC) and atomic absorption spectroscopy (AAS) using a sample amount as low as 50-100 mg. The outlined procedure can be successfully applied to routine work, thus obtaining suitable information about a sample's chemical composition. This helps to attribute or exclude common sources of separate specimens.

Drug profiling: a new scientific contribution to law enforcement operations in Viet Nam have studied by Hung HM et al. (2005) [18]. Heroin sample since 2005 comparisons have been carried out in Viet Nam have established links between wholesalers and retailers. In this study physical and chemical characteristics, packaging material, including fingerprints of diacetylmorphine (heroin) content and the composition of some main alkaloids have been carried out. A total 375 heroin and 29 methamphetamine samples have been analyzed for major and minor impurities. Substances detected in the analysis of illicit heroin include diacetylmorphine, morphine, codeine, 6-monoacetylmorphine and acetyl codeine as well as paracetamol and caffeine and methamphetamine impurity profiling began, 29 samples have so far been analyzed. Impurity profiling has established a link between two major trafficking groups suspected of obtaining heroin from the same source of production. In addition, impurity profiling provides new information on the preparation and production of some methamphetamine and fake Ecstasy tablets.

The identification of the components can give valuable information on the drug provenance. Several techniques have been used to analyse the components in street heroin samples, with GC-MS being by far the most widely used analytical technique (Zhang D et al., 2004) [4]. The GC-MS is considered a "gold standard" for forensic substance identification, as it is used to perform a specific test, which positively identifies the actual presence of a particular substance in a given sample.

In the present study, analysis of exhibits seized from different sources was carried and link between various sources was tried to establish based on cutting agents and impurities profiling by using various techniques and method for the best separation and identification of the illegal drugs.

In forensic drugs analysis, the exhibits submitted for examination are very likely to show significant variation both in their physical/appearance form and chemical composition and not all methods described in this study for detection of heroin and other adulterants/constituents present in the exhibits. The choice of the methodology and approach to determine the constituents' various techniques are used. These techniques are able to determined and confirm the constituents in the exhibits.

Methodology

Sixty Seven seized illicit drug samples, were taken for detection of various constituent these samples recieved during the period from June 2018 to December 2018.

Methods provided here are chosen on the basis of proven suitability and reliability, important prerequisites, especially if the results are to be used for evidential purposes. Since similarity based on one method alone is usually not sufficient for evidential purposes and in order to make the overall process more rigorous, hence it is important at least a second method have applied where each method used addresses a different set of target analytes.

Experimental

Material and Methods

All chemicals were used of high purity E Merck. The samples were recived from the investigating agencies during the said period of time.

Colour and Texture of the Samples

These samples were in the form powder and granules having different hue and colours viz. white, off white, light brown, dark brown, pink and orange colour. The colour of the samples may be due to presence of cutting agent or intermediate products or impurities.. The following tests were carried out for establishing various cutting agents present in the contraband drugs.

Figure 2: Samples of Heroin with impurities and cutting agents

Colorimetric Spot Tests

Colorimetric spot tests are used in forensic casework in order to quickly screen a sample prior to more discriminating tests. Using a spot test or a series of spot tests, can determine whether or not a certain drug of abuse may be present. This allows making a wise decision moving forward in the analysis. With a limited amount of sample is required to determine the nature and identity of the compounds. These tests are only preliminary tests, which tell the certain drug may be present.

S. No.	Alkaloids	Marquis	Mecke	Frohde
1.	Heroin	Purple violet	Dark green	Purple become grey/purple
2.	Morphine	Purple violet	Dark green	Purple become grey/purple
3.	6-Monoacetylmrphine	Purple violet	Dark green	Yellow green
4.	Acetylcodeine	Purple violet	Dark green	Purple become paler

Table 1: Spot tests for Heroin and Opiates

S. No.	Adulterants/drugs	Ferric Chloride	H2SO4	Amalic Acid test	Zwikkers test	Lieberman's
1.	Caffeine	-	-	Orange	-	-
2.	Dextromethorphan	-	-	-	-	Black
3.	Phenobarbital	-	-	-	Violet	Red orange
4.	PCM	Blue	-	-	-	Violet

Table 2: Spot tests for Additives/Adulterants

Mandelin Reagent: Dissolve 1.0 g of ammonium vanadate in 100 mL of concentrated sulfuric acid.

Marquis Reagent: Carefully add 100 mL of concentrated sulfuric acid to 5 mL of 40 percent formaldehyde (v/v, formaldehyde: water).

Nitric Acid: Concentrated Nitric acid.

Ferric Chloride: Dissolve 2.0 g of anhydrous Ferric Chloride or 3.3 g of Ferric Chloride Hexahydrate in 100 mL of distilled water.

Frohde reagent: Dissolve 0.5 g of Molybdic acid or Sodium Molybate in 100 mL of hot concentrated sulfuric acid.

Mecke Reagent: Dissolve 1.0 g of Selenious acid in 100 mL of concentrated sulfuric acid.

Zwikker Reagent: Solution A: Dissolve 0.5g of Copper (II) Sulfate Pentahydrate in 100 mL of distilled water. Solution B: Add 5 mL of pyridine to 95 mL of Chloroform. Procedure: Add 1 volume of solution A to the drug, followed by 1 volume of solution B.

Simon's Reagent: Solution A: Dissolve 1 g of Sodium Nitroprusside in 50 mL of distilled water and add 2 mL of acetaldehyde to the solution with thorough mixing. Solution B: 2 percent Sodium Carbonate in distilled water. Procedure: A Add 1 volume of solution A to the drug, followed by 2 volumes of solution B.

Thin Layer Chromatography

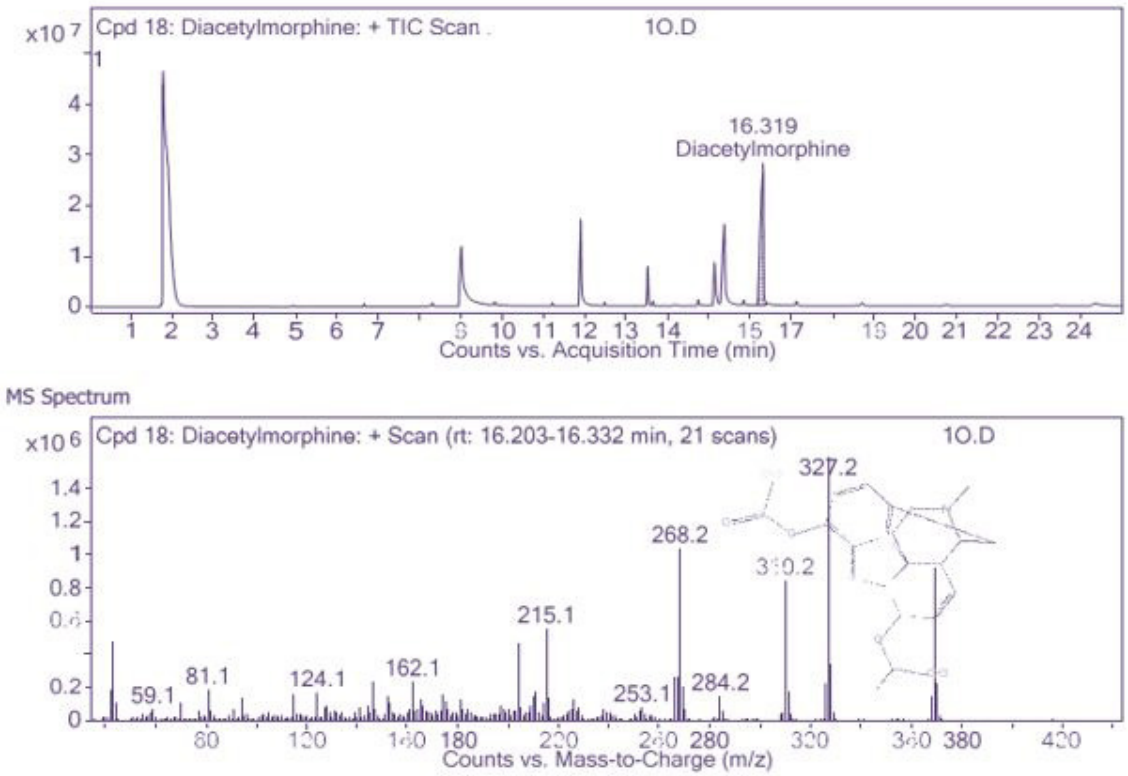
This method is very rapid, sensitive and amenable to a wide range of substance visualization techniques and also it is cost effective. TLC is commonly used in routine screening procedures, and subsequent confirmatory analysis usually involves a more sensitive and sophisticated chromatographic technique such as GC and GC-MS. The TLC plate is coated with silica gel G at thickness of 0.25 mm. In this experiment TLC plates from E Merck and various constituents present in the heroin sample have been screened. The solvent systems were used detection of Diacetylmorphine, morphine, caffeine, acetaminophen, phenobarbital, alprazolam and dextromethorphan etc. solvent systems have been selected as per the presence and nature of the constituents.

Results

A total 67 Heroin/smack/ brown sugar samples were received during the period of June 2018 to December 2018. In this contraband contains less than 50% of the total samples contains only Diacetylmorphine, other samples contains more than one cutting agent. The constituent have been confirmed by GC-MS Diacetylmorphine (fig:3), caffeine(fig:5), acetaminophen(fig:7), phenobarbital(fig:9), dextromethorphan(fig:8) acetylcodiene(fig:6) present as impurity and monoacetyl morphine (fig:4). The details of combination of cutting agents and impurities profile of the seized drugs are given in the table 3.

S.No.	Constituents present in the seized drugs	No. of samples
1.	Diacetylmorphine (DAM)	32
2.	Diacetylmorphine+Monoacetylmorphine+Acetylcodiene	07
3.	Dieacetylmorphine+Monoacetylmorphine+Acetylcodiene+Alprazolam	02
3.	Diacetylmorphine+Monoacetylmorphine+Acetylcodiene+PCM	04
4.	Diacetylmorphine+Monoacetylmorphine+Acetylcodiene+ Caffeine	02
5.	Diacetylmorphine+Monoacetylmorphine+Acetylcodiene+PCM+ Caffeine	04
6.	Diacetylmorphine+Monoacetylmorphine+Caffeine+PCM Dextromethorphan	04
7.	Diacetylmorphine+Monoacetylmorphine+ Acetylcodiene+Caffeine+ Dextromethorphan	02
8.	Diacetylmorphine+Monoacetylmorphine+Acetylcodiene+ Caffeine+PCM+Dextromethorphan	02
9.	Diacetylmorphine+Monoacetylmorphine+Acetylcodiene+PCM+ Alprazolam+Phenobarbital	03
10.	Diacetylmorphine+Monoacetylmorphine+Acetylcodiene+Caffeine+ Dextromethorphan+PCM	02
11.	Diacetylmorphine+Monoacetylmorphine+Acetylcodiene+ Alprazolam +PCM	03

Table 3: Diacetylmorphine, Monoacetylmorphine, Acetylcodiene and Cutting agents detected in the number of samples



GC-MS Spectra of the detected compounds

Figure 3: MS-Spectra of Diacetylmorphine

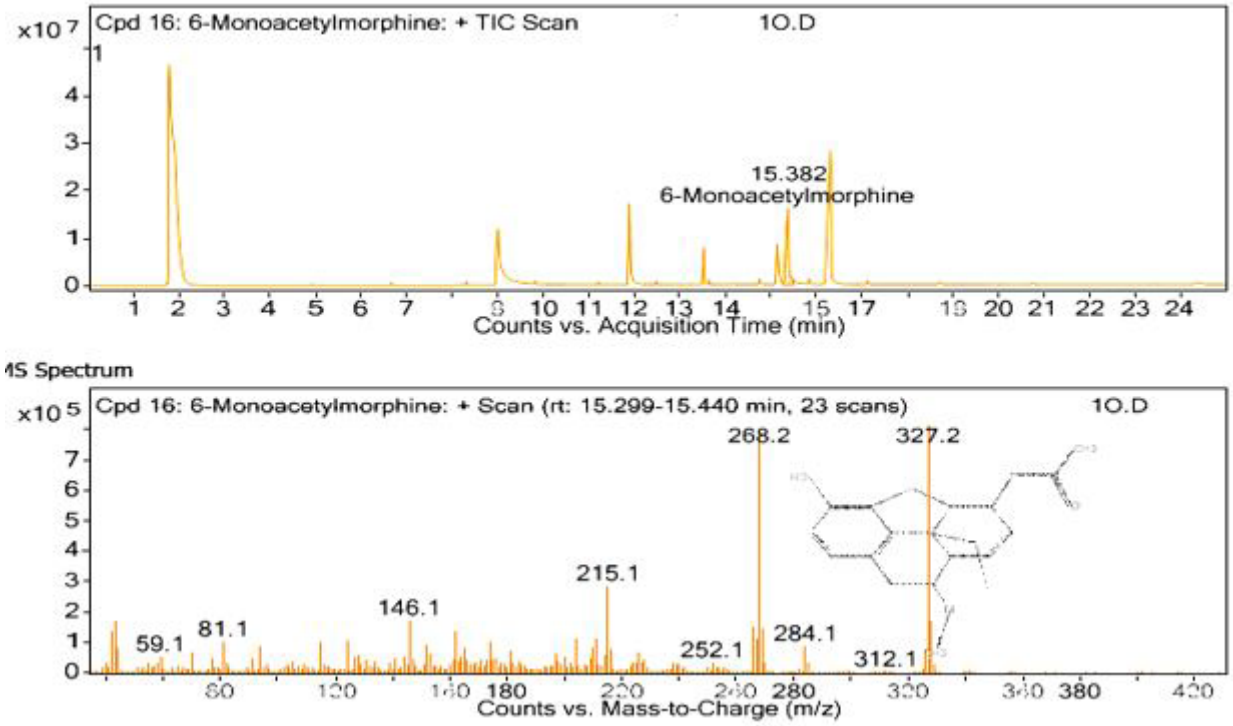


Figure 4: MS-Spectra of Monoacetylmorphine

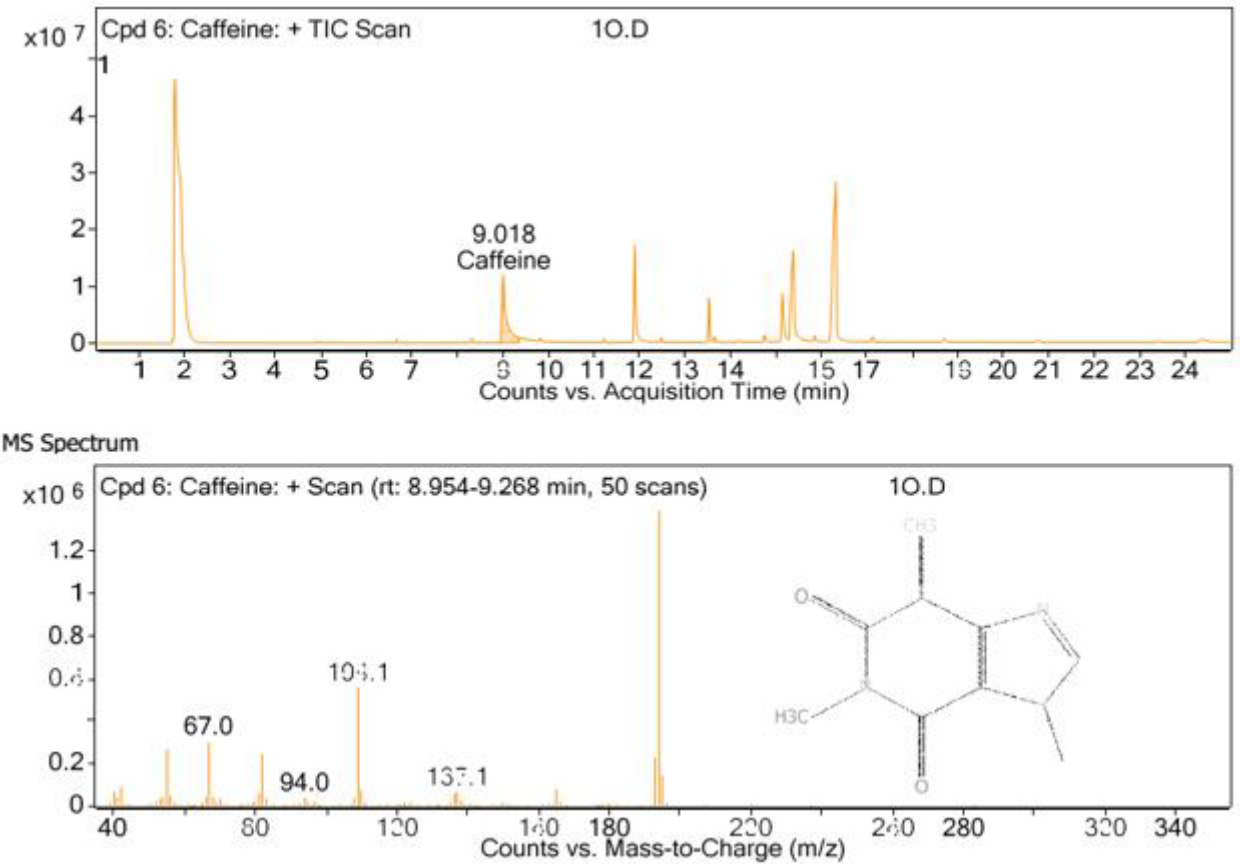


Figure 5: MS-Spectra of Caffeine

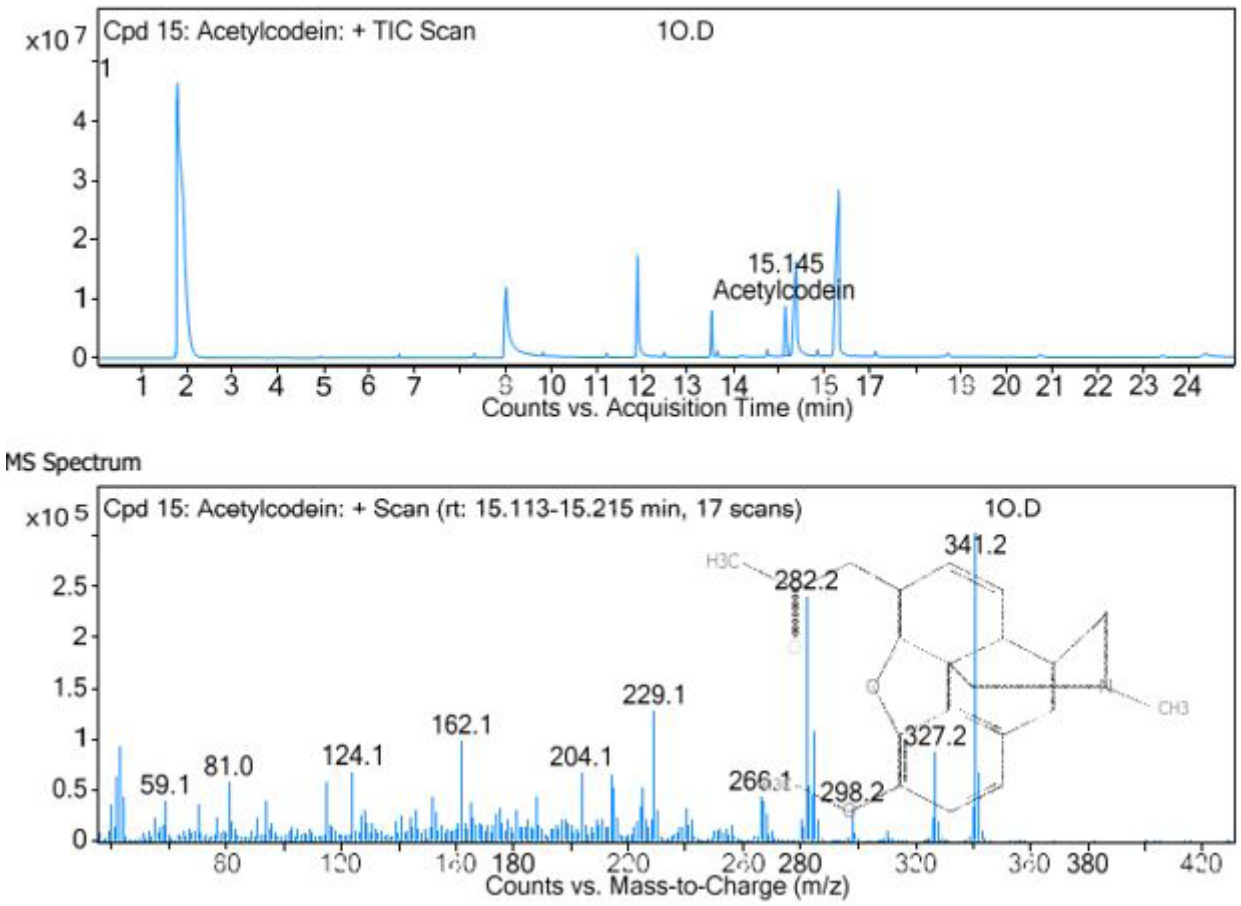


Figure 6: MS-Spectra of Acetylcodein

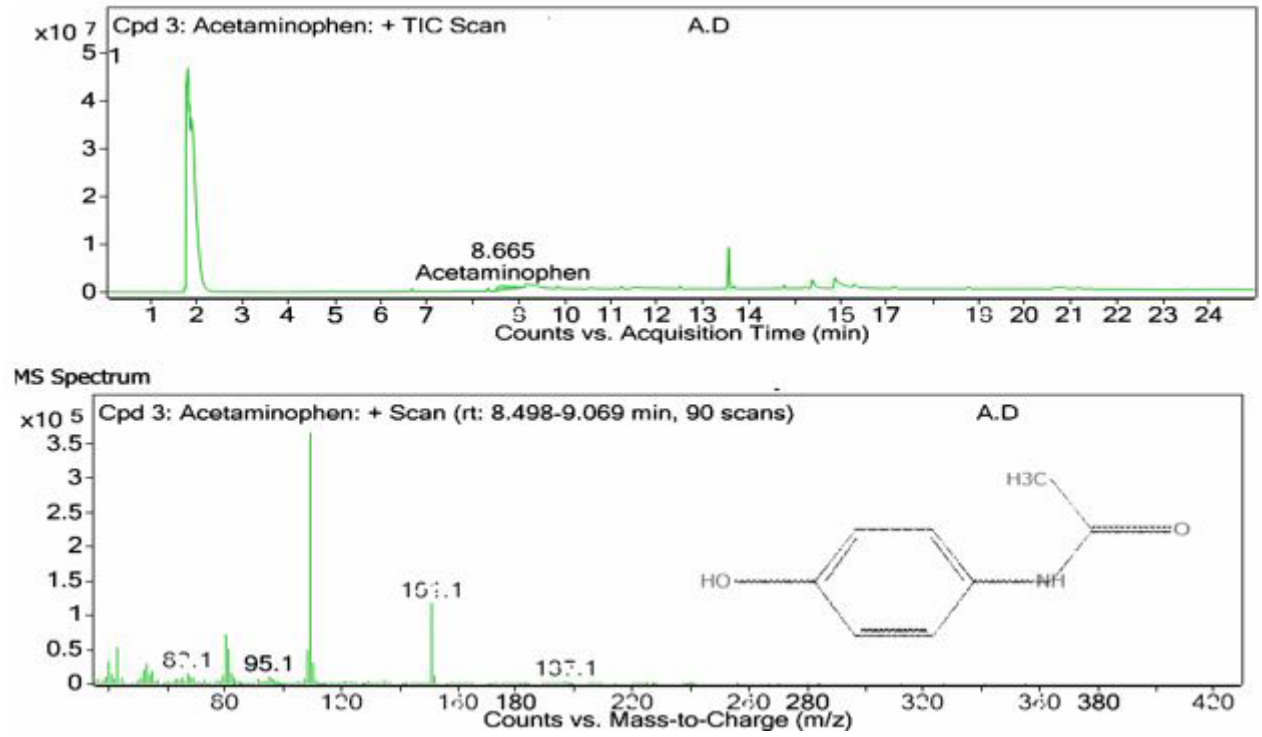


Figure 7: MS-Spectra of Acetaminophen

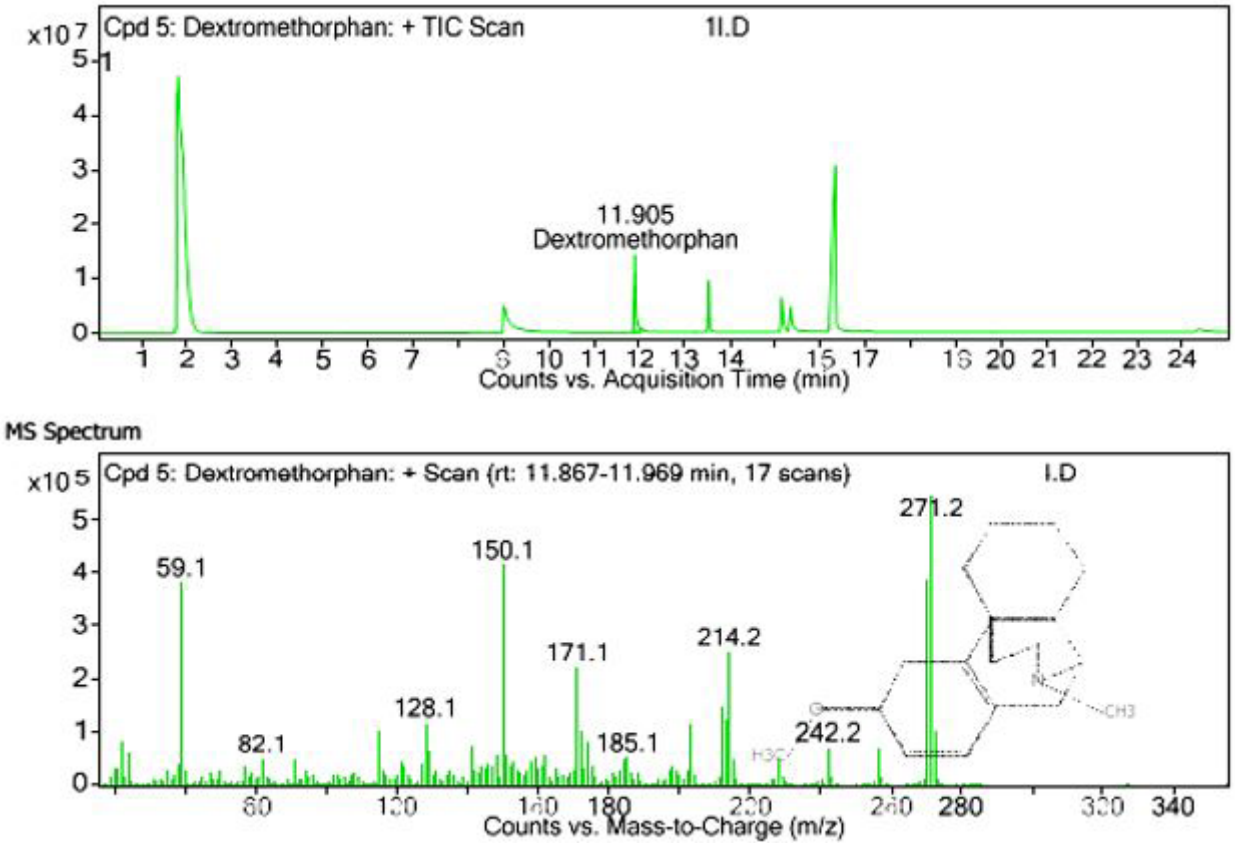


Figure 8: MS-Spectra of Dextromethorphan

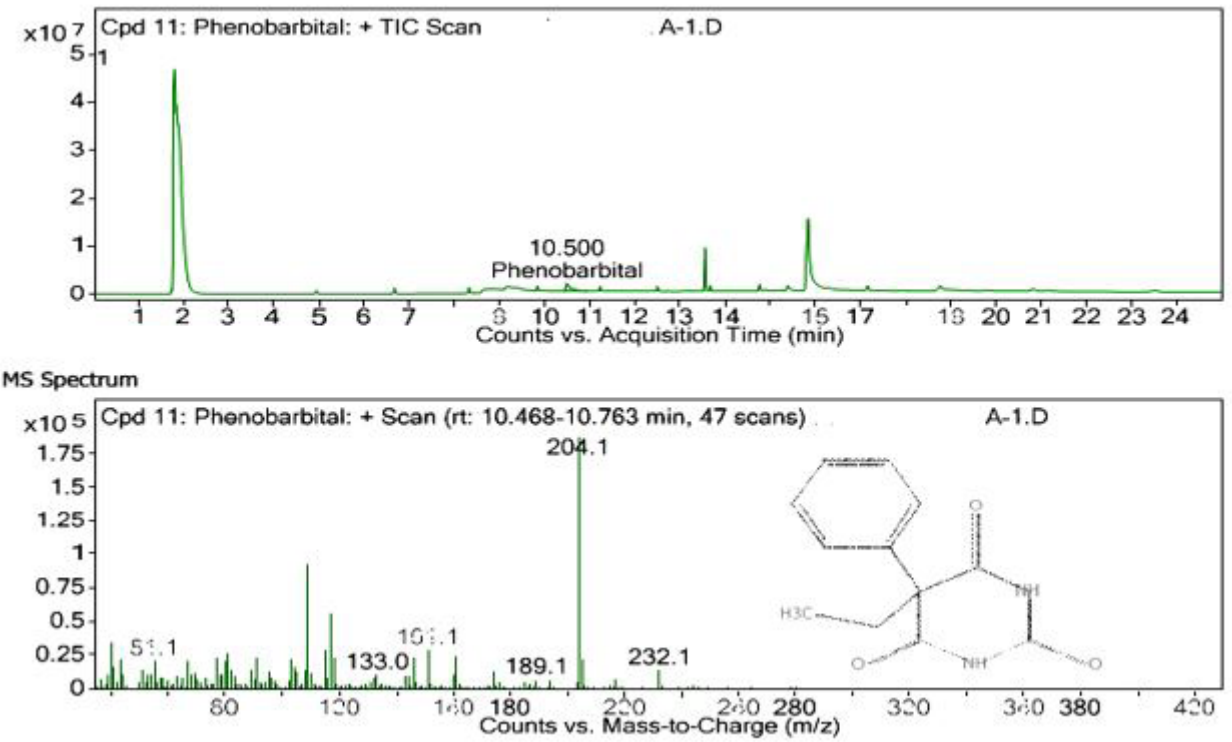


Figure 9: MS-Spectra of Phenobarbital

Conclusion

Cutting agents are added very meticulously so as to feign the same effects as that of a molecule and also reducing the effective cost and serving same or more benefits than the parent compounds. It has been concluded that the Caffiene, Dextromethorphan, Paracetamol, Alpazolam and Phenobarbital the new class of compounds found commonly added as cutting agents in the heroin samples whereas acetylcodiene present as impurity and monoacetylmorphine as intermediate product of diacetylmorphine. Finally the drug characterization and impurity/adulterants profiling in the research was helpful to investigating agencies for provide supporting evidence in cases where illicitly manufactured drugs has the same source or otherwise, it also helps the law enforcement can pursue criminal charges and the court can determine appropriate sentencing. The analytical techniques are used in the study are best enough determine the each constituents presnt in the heroin samples.

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