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CHEMICAL ANALYSIS OF ILLICIT TABLETS FROM FORENSIC SCIENCE SERVICE SEIZURE

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ABSTRACT

Ecstasy is the common name for illicit street drugs that contain 3,4-methylenedioxy-methamphetamine (MDMA) or 3,4-methylenedioxymethamphetamine hydrochloride (MDMA.HCl) as the active ingredient. It has a number of effects on the user from affecting mood to disrupting brain and liver functions. There are a number of impurities in ecstasy tablets which are present due to the synthesis route used or the addition of other ingredients that may enhance or dampen the effect of MDMA when consumed. Raman spectra and PXRD diffractogram results showed that none of the samples analysed contained MDMA despite being marketed as such; therefore, user of ecstasy are exposing themselves to other chemical compounds that are potentially harmful to them.

Keywords: *ecstasy, MDMA, empathogen, profile, tablet composition, impurities.*

INTRODUCTION

Ecstasy, also known as E, X, XTC, Molly, Adam, Essence is a drug sold in the illicit market. Ecstasy is produced in clandestine laboratories in Western European countries like Netherlands, Belgium, and Germany [1]; despite restrictions by the EU (European Union) on its precursors. The tablets come in a variety of aesthetically pleasing colours with stamps/brands [2]. Ecstasy became popular in raves and techno parties in the 1980's similar to other amphetamines, lysergic acid diethylamide and psilocybin [1]. The active compound in ecstasy tablets is 3,4-methylenedioxymethamphetamine (MDMA), a ring-substituted amphetamine first synthesised by Merck Chemist Anton Köllisch in 1914 while trying to improve the compounds available to prevent haemorrhage [2]. MDMA belongs to the amphetamine class of psychoactive hallucinogen. Compared to the parent compound – MDA (methylenedioxyamphetamine), MDMA is not a hallucinogen but is placed in a new class of drugs called empathogens because of its ability to break down barriers between people, thus making them trust each other. With no medical use, it was once considered for couples' therapy [3].

MDMA has the molecular formula - $C_{11}H_{15}NO_2$ but is also found as a hydrochloride salt ($C_{11}H_{15}NO_2$.HCl) [2] in ecstasy tablets. An average oral dose of 100mg of MDMA can be felt 30 to 45 minutes after ingestion, peaking in 60 to 90 minutes and lasting between 6 to 8 hours, however, full recovery from the drug can take up to 3 days [1]. Street tablets may contain between 2 and 105mg of MDMA in tablet weighing about 200 to 300 grams [4]. This difference in the

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quantity of MDMA in ecstasy tablets indicates that there are other ingredients, impurities and additives that are ingested. Ecstasy users typically experience loss of appetite, grinding of teeth, muscle ache/stiffness, ataxia (lack of coordination), exhaustion, "flashbacks", paranoia [5], elevated anxiety, papillary dilation [6]. Higher doses (>200mg) of MDMA elicit acute effects such as nausea, confusion difficulty in reasoning, speaking and concentrating, with brain haemorrhaging and heart failure occurring in users with poor health. Body temperature of the user also rises up to 47°C with damage to nerve cells, deterioration of muscular system, nephrotoxic and hepatotoxic. Its consumption likely increases the risk of cancer (in certain individuals with a gene mutation) as well as hepatic (by oxidation) and neurological complications [7]. Tolerance to ecstasy can occur with habitual use caused by piggybacking or stacking [1]. MDMA also induces polydipsia (excessive thirst) [8], thereby causing brutal and sometimes deep hyponatraemia due to sweating and excess water intake [9]. Polydrug abuse can affect the effects experienced by ecstasy users as it used in conjunction with alcohol [10], marijuana and methamphetamine [11]. Up to 70% of ecstasy users co-abuse alcohol and ecstasy [12], [13] and [14]. The impurities and by-products in ecstasy tablets have different origins due to the different synthesis pathways, quality of chemicals/precursors used, the drying, crystallisation and tabletting processes [15]. There is no quality control or quality assurance during illicit drug manufacture and ecstasy users need to be aware of this as they are exposed to all sorts of potentially toxic compounds [16]. This paper describes the analysis and results of street samples of ecstasy.

MATERIALS AND METHODS

Eight (8) batches of small sample size from a larger seizure made by the Forensic Science Service (FSS), United Kingdom were selected. The samples, dated as approximately three months old, were identified as A21, P3, P4, P7, P11, P23, P28, P30 as shown in Table 1.

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Table 1. Details of 8 batches of tablets analysed.

Sample	Brand	Appearance	
		Colour	Shape
A21	LOVE/LOTE	White.	Round/Circular.
P3	Crown	Light brown with dark brown.	Round/Circular.
P4	Euro	Cream.	Round/Circular.
P7	Playboy	Cream.	Round/Circular.
P11	Pink heart	Light pink.	Heart.
P23	Orange	Orange.	Granular.
P28	Creamfields	Cream.	Round/Circular.
P30	Superman	Off white.	Round/Circular.

Raman spectroscopy was carried out on the ecstasy samples using Renishaw inVia Raman Microscope coupled to a Charge Coupled Device (CCD) cooled nitrogen gas detector with a 785nm laser, at 50× magnification, calibrated with silicon at 520.412 ± 0.255 cm^{-1} with GRAMS/AI software used for spectral analysis. Powder x-ray diffractograms (PXRD) were captured using Bruker D8 Advance diffractometer, analysed using EVA software. Raman spectra and x-ray diffractograms of samples were compared to standard MDMA.HCl. The active substance and excipients were measured and matched based on library searches on both equipment.

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RESULTS AND DISCUSSION

Raman spectroscopy indicated the presence of various compounds in the samples, as detailed in Table 2.

Table 2. Compounds present in each tablet using Raman Spectroscopy.

Sample	Brand	Active substance
A21	LOVE/LOTE	diphenhydramine (DPH), methyl salicylate.
P3	Crown	3,4-methylenedioxyethylamphetamine (MDEA), benzylpiperazine (BZP), trifluoromethylphenylpiperazine (TFMPP).
P4	Euro	dextromethorphan (DXM).
P7	Playboy	DXM, pseudoephederine/ephedrine.
P11	Pink heart	Caffeine.
P23	Orange	Pseudoephederine/ephedrine, methyl salicylate, phenylcyclohexylpiperidine (PCP), caffeine.
P28	Creamfields	-
P30	Superman	BZP, TFMPP, di-BZP, DPH, ketamine.

PXRD diffractograms of ecstasy tablets as depicted below in Figures 1. to 8.

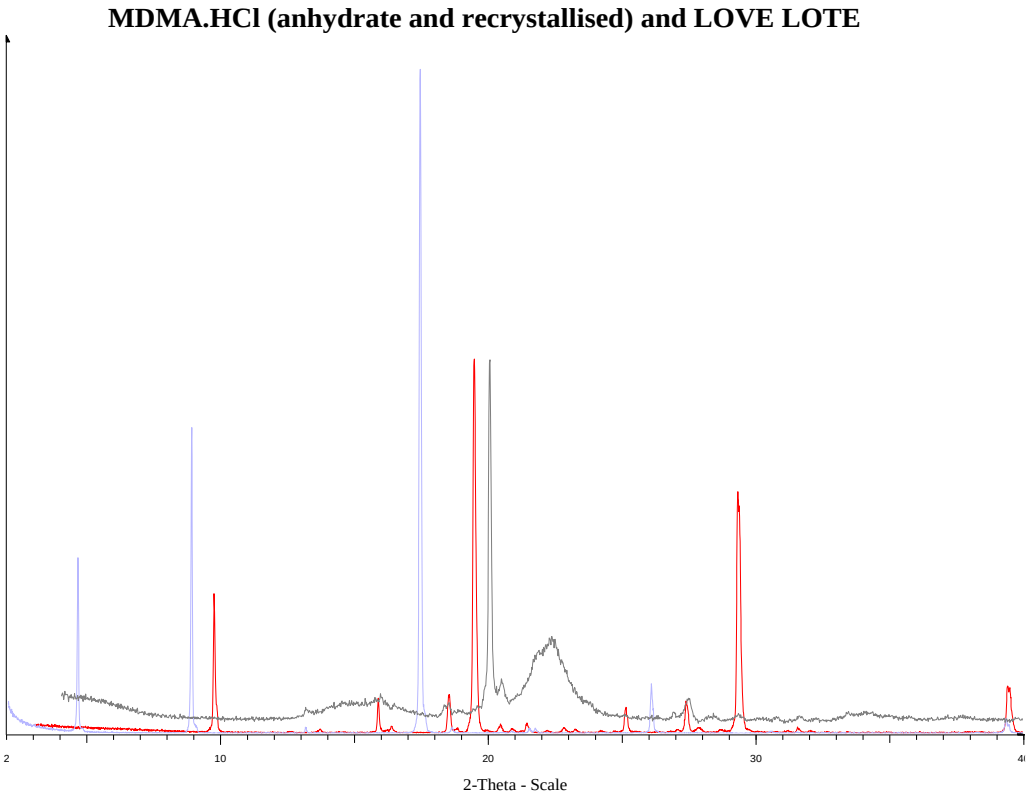

Figure 1. Diffractogram of MDMA and A21

ISSN 0795 - 22066

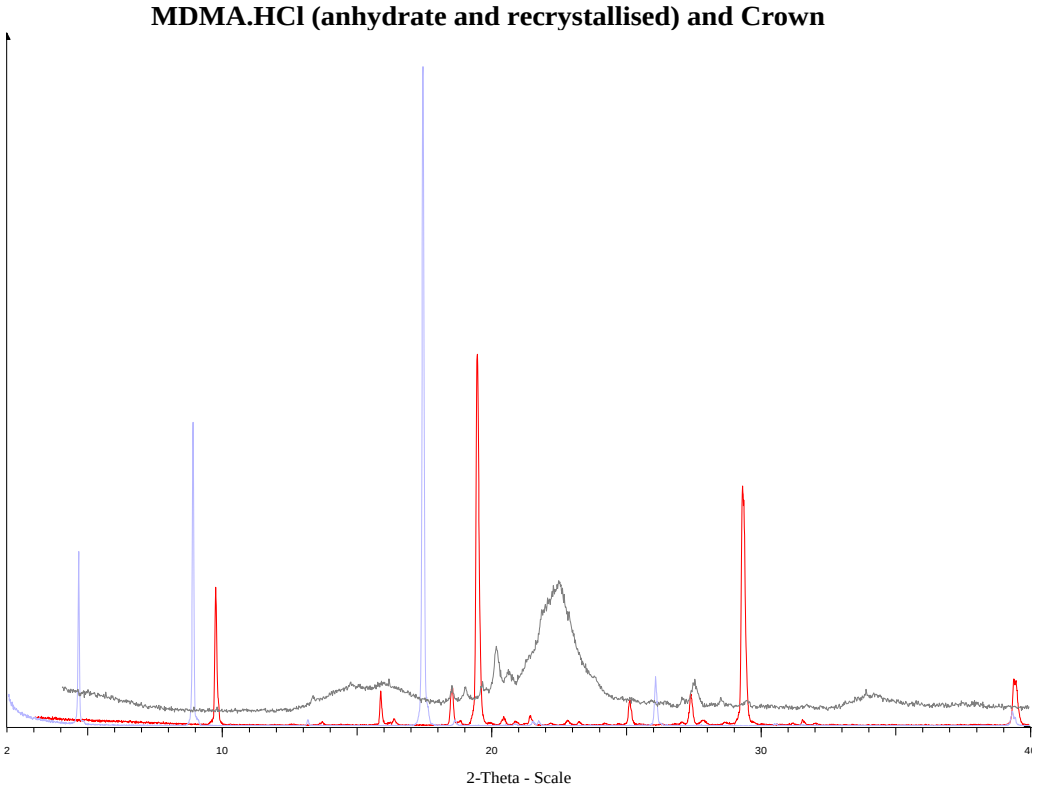

Figure 2. Diffractogram of MDMA and P3

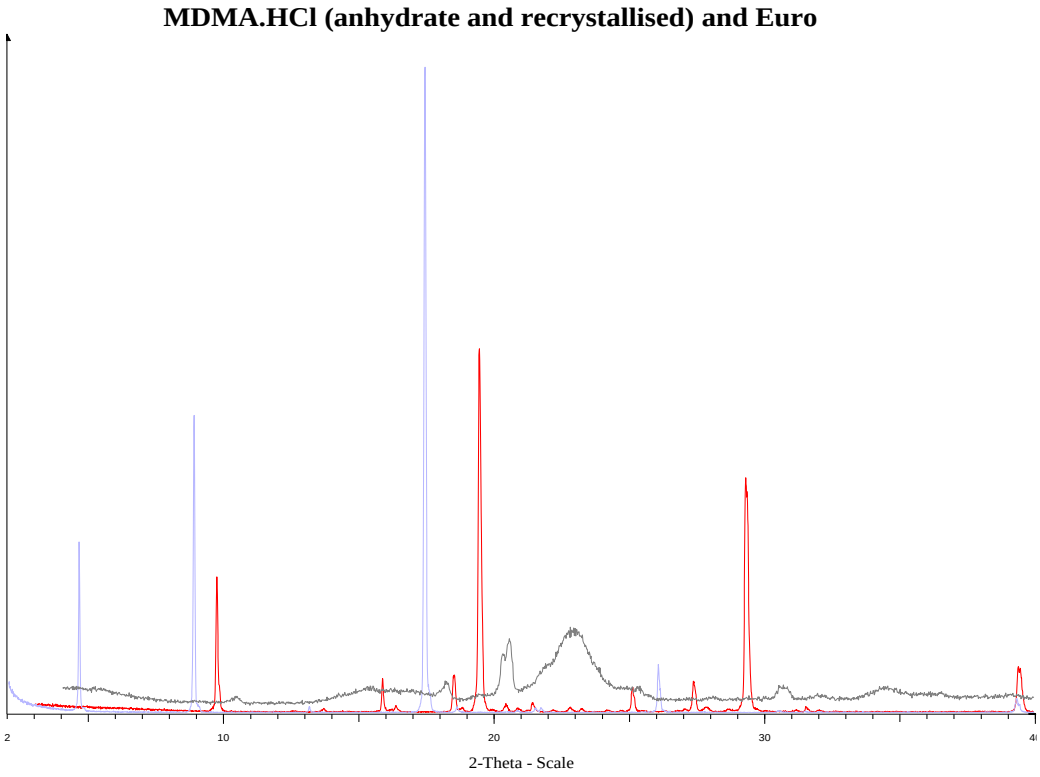

Figure 3. Diffractogram of MDMA and P4

ISSN 0795 - 22066

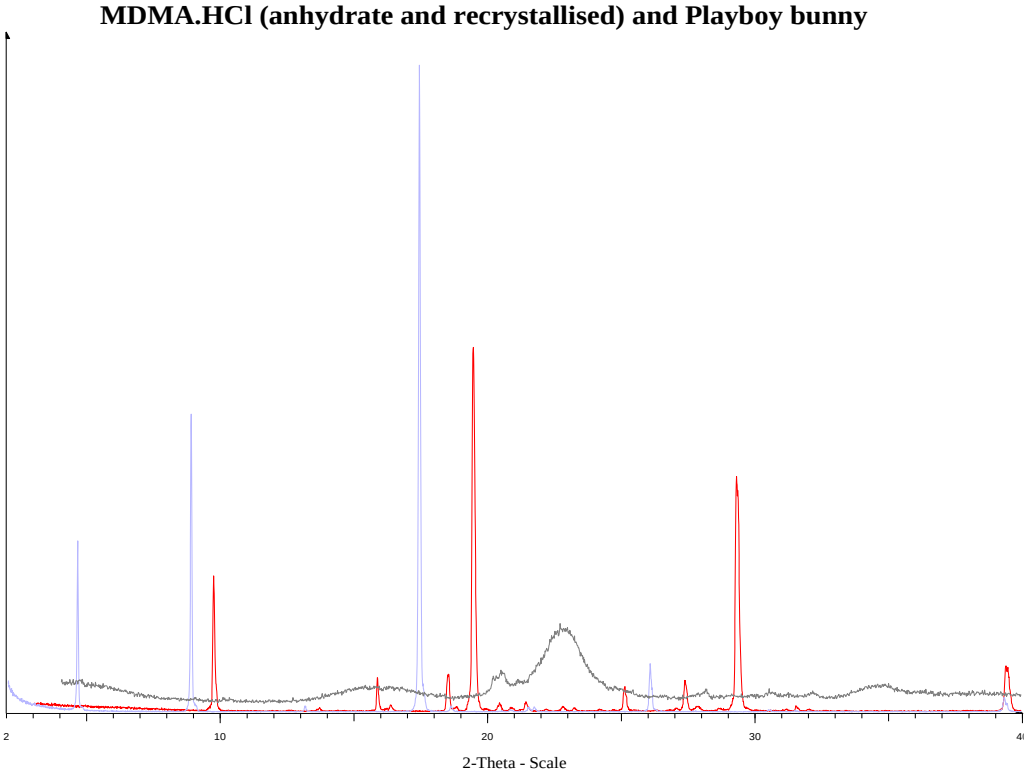

Figure 4. Diffractogram of MDMA and P7

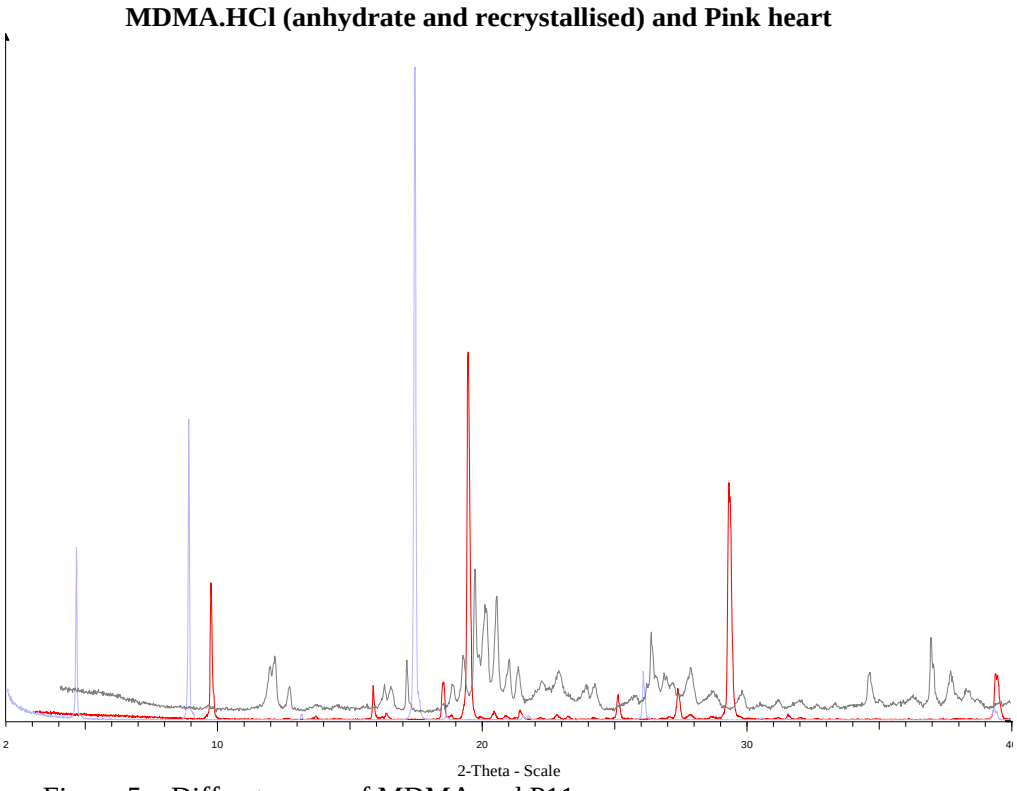

Figure 5. Diffractogram of MDMA and P11

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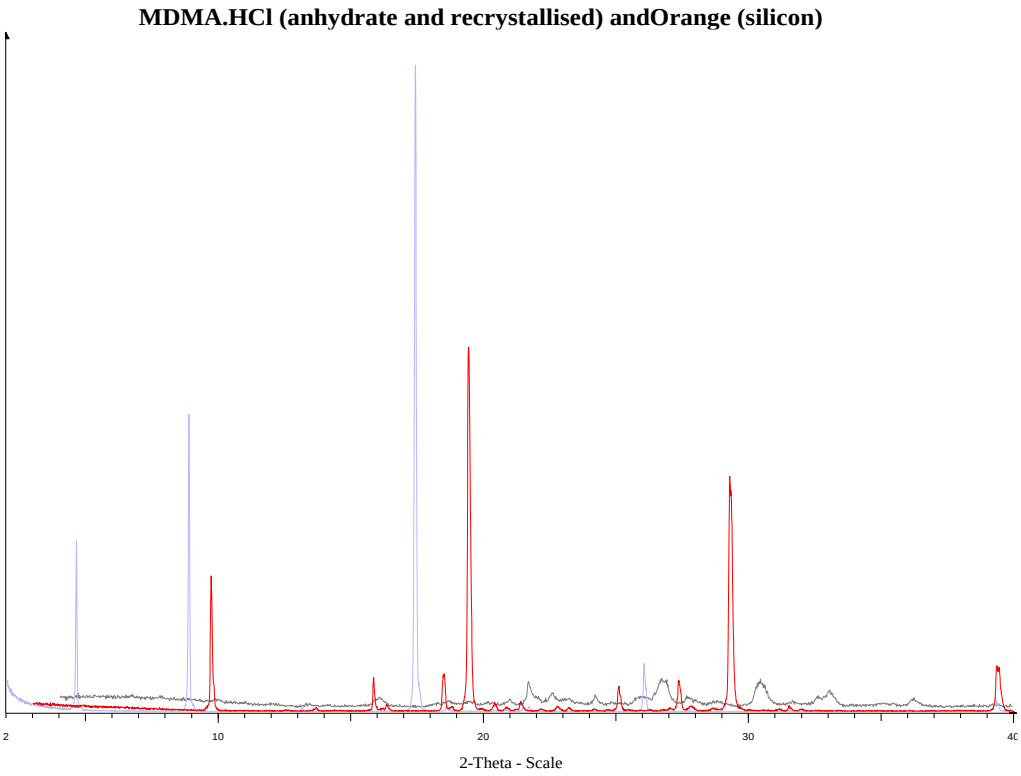

Figure 6. Diffractogram of MDMA and A23

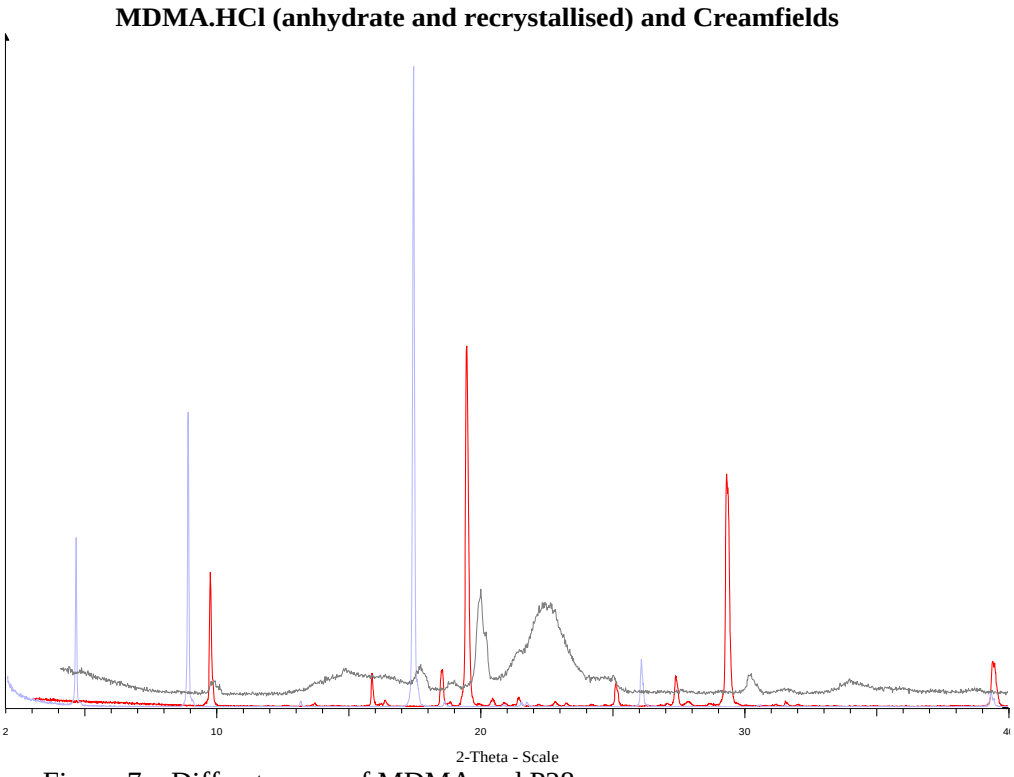

Figure 7. Diffractogram of MDMA and P28

ISSN 0795 - 22066

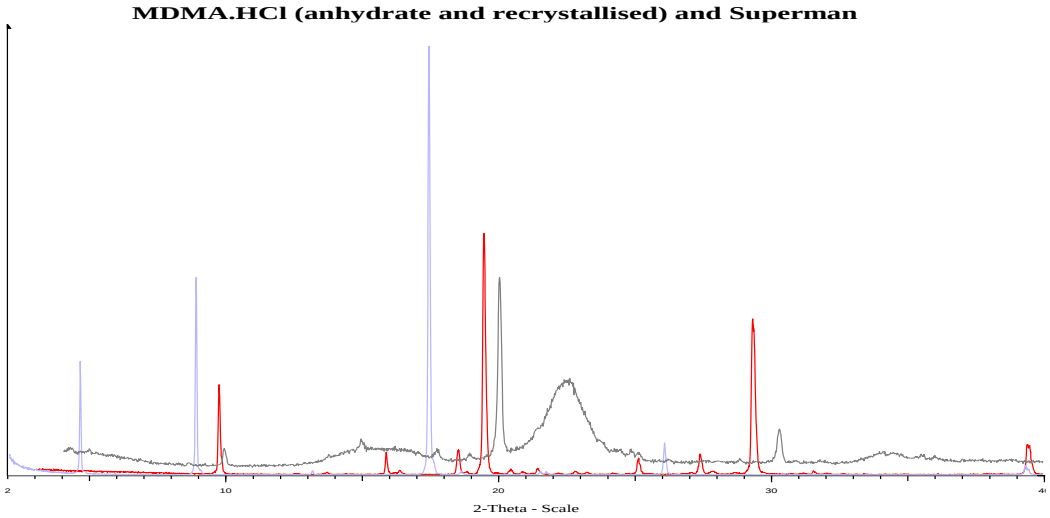

Figure 8. Diffractogram of MDMA and P30

DISCUSSION

From the results of the Raman and PXRD analyses, all the tablets labelled as ecstasy did not contain the expected active ingredient – MDMA or its chloride salt. This indicates that their physical characteristics shows no correlation with the composition of the tablets. This indicated that the tablets contain chemical compounds that make the effects of the drugs multiplied. These compounds are dangerous to human health and have the potential to cause death. Hence, the tablets were rearranged as follows, according to the toxicity of the compounds they contain.

Table 3. Compounds present in each tablet based on toxicity.

Sample	Brand	Active substance
P30	Superman	BZP, TFMPP, DBZP, DPH, ketamine.
A21	LOVE/LOTE	DPH, methyl salicylate
P3	Crown	MDEA, BZP, TFMPP
P23	Orange	methyl salicylate, PCP, caffeine, pseudoephederine/ephedrine
P7	Playboy	DXM, pseudoephedrine/ephedrine
P4	Euro	DXM
P11	Pink heart	Caffeine
P28	Creamfields	-

ISSN 0795 - 22066

DPH is an antihistamine also used against vomiting and nausea with a minimum lethal concentration of 5µg/ml or at most 1g. Symptoms such as drowsiness, tachycardia, hallucinations, confusion, convulsions, delirium, rhabdomyolysis, coma can be observed when 50-60mg of DPH is consumed [17]. There are more cases of death caused by DPH than the other compounds in the table above due to its high toxicity.

Death can occur when 19.8 – 57mg pf DXM is ingested [18]. DXM is an antitussive found in OTC (over the counter) cough medication. It is a morphine derivative and when consumed in excess causes euphoria, hallucinations, perceptual awareness, altered time perception, slurred speech, sweating and hypertension [19].

More than 10mg of PCP can induce a coma that can be fatal [20]. Ketamine is a potent anaesthetic that causes results in impaired attention, learning ability memory in small doses. Higher doses of 1g cause delirium, amnesia, impaired motor function, high blood pressure, depression and potentially fatal respiratory problems when administered intravenously. PCP is structurally like ketamine, so produce similar effects when ingested [21].

Caffeine is a stimulant which also increases the release of dopamine in the brain and acts similarly to amphetamines and cocaine but in a limited capacity. When ingested in conjunction with MDMA, it increased tachycardia and core body temperature, long term brain damage and eventually causing death [22].

The minimum lethal quantities of pseudoephedrine/ephedrine, methyl salicylate, and MDEA are much larger than the other compounds because of their shorter half-life, their use in pharmaceuticals.

Methyl salicylate is found in pain medication and toxic when ingested and can lead to loss of vision, nausea, vomiting, convulsions, kidney failure, difficulty breathing and hallucinations [23]. MDEA is also an empathogenic psychoactive drug and acts by increasing the release of dopamine, similar to MDMA, thus, it produces similar effects to MDMA

Ephedrine and its isomer pseudoephedrine are CNS stimulants that cause high blood pressure by increasing heart rate and vasoconstriction.

BZP and TFMPP have similar effects. BZP has amphetamine-like effects, TFMPP has ecstasy-like effects, hence, they both entactogenic; however, they potentially cause anxiety, headaches, nausea, insomnia, toxic seizures and heart palpitations [24]. They are not nearly as fatal as the other compounds, despite what the user experiences. The effects of ingesting 130mg are completely absent after about 7 hours. They

DBZP on the other hand is an impurity formed during improper synthesis of BZP, but its effects are not clearly understood [25].

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It should be noted that where compounds such as DXM, ketamine, caffeine and MDEA are found in conjunction with MDMA, they act synergistically to amply the effect of MDMA, hence can easily be fatal. Some of these are yet to be classified under the Controlled Substances Act (CSA), and could in theory become more widely abused due to lack of data, are not on the list of drugs that must be confiscated during transportation.

CONCLUSION

The European Monitoring Centre for Drug and Drug Addiction in 2007 stated that there is growing trade in BZP/TFMPP pills in Europe with 13 EU Member States reporting seizures. Hence, the detection instruments at airports should be employed to detect for such drugs, not just the common ones such as cocaine, marijuana, heroin and ecstasy. This report is limited to the use of ecstasy in the EU, however, ecstasy is also widely consumed in North America.

In Nigeria, though ecstasy is not the dominant choice for drug abuse, its equivalent is marijuana or tramadol, though their modes of action are different. If confiscated tablets should be characterised before destruction to identify the active ingredient is such tablets. Both ecstasy and marijuana contribute to the increase in unacceptable behaviour and potential transmission of diseases largely due to the empathogenic nature of MDMA.

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