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Crystals and tablets in the Spanish ecstasy market 2000–2014: Are they the same or different in terms of purity and adulteration?

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ABSTRACT

Background: Although 3,4-methylenedioxymethamphetamine (MDMA) has a long history in recreational settings, research on its composition (purity and adulteration) has focused only on tablets even though crystal format is readily available for users.
Methods: Drug specimens collected between January 2000 and December 2014 were analyzed at Energy Control's facilities. All samples were voluntarily provided by drug users. Sample identification was made with thin layer chromatography and gas chromatography coupled to mass spectrometry, and quantification with ultraviolet spectrophotometry (only in unadulterated samples).
Results: Between January 2000 and December 2014, 6200 samples purchased as ecstasy by their users were analyzed. Crystals were the most frequent format (60.6%) followed by tablets (38.8%). During the study period, the proportion of samples containing only MDMA was higher in crystals than in tablets. Compared with tablets, adulterated crystal samples contained the same number of adulterants but more combinations of different substances. Although caffeine was commonly detected as adulterant both in crystals and tablets, other substances such as phenacetin, lidocaine, dextrometorphan or methamphetamine were detected almost exclusively in crystal samples. The amount of MDMA in crystal samples remained stable unlike tablets for which a huge increase in MDMA dose was observed since 2010.
Conclusion: Crystal samples of ecstasy showed clear differences compared to ecstasy tablets and this must be taken into account both in research and harm reduction.

1. Introduction

MDMA (3,4-methylenedioxymethamphetamine) has a long history in recreational settings and several studies have documented its composition in samples sold as ecstasy. In the Netherlands, in over two decades, more than 100,000 samples of controlled drugs have been analysed [1] and several scientific papers about MDMA composition have been published [1–5]. During a period of 16 years, the Drugs Information Monitoring System (DIMS) in the Netherlands analysed the content of 33,006 tablets sold as ecstasy that were handed in by numerous individual (potential) substance users. Their results showed that the number of high-dose tablets (≥106 mg MDMA per tablet) gradually increased from 1998 to 2008. The same holds true for the proportion of tablets that contained only MDMA, reaching the highest levels in 2000 and 2004. After 2004, the purity of ecstasy decreased again, caused mainly by a growing proportion of tablets containing meta-chlorophenylpiperazine (mCPP) [2].

Data about MDMA composition has been also published by the French National Identification System for Drugs and Other Substances (SINTES). Between July 1999 and June 2004, 9453 samples were analysed. Tablets (7004) mainly contained MDMA (82%), and caffeine was the most frequent blended psychoactive substance. Mean MDMA dosage of tablets decreased from 1999 to 2003 [6]. In UK, 101 Ecstasy tablets seized from individuals attending nightclubs were analysed qualitatively to determine if they contained MDMA and quantitatively to determine the MDMA content per tablet [7]. The mean amount of MDMA hydrochloride

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was 58.7 + 22.9 mg per tablet, with a range of 20–131 mg. The majority (96.0%) of tablets contained less than 100 mg MDMA.

Recently, crystal format has become the most common presentation for MDMA in several European countries [8]. Although the exact reasons for this shift remain unknown, some authors have pointed out towards the decreased purity of MDMA tablets [9] or the convenience of crystal for manufacturers and distributors: the need of a tablet press could be avoided and crystals need less space than tablets to transport the same quantity of the drug [10]. Moreover, this format has prompted new forms of consumption which could imply additional risks to users. Some of these include dabbing MDMA crystal from packets with a moistened finger, making "bombs" out of cigarette papers, and snorting the powder either alone or mixed with other drugs such as cocaine, amphetamines, and ketamine in "designer lines" [9]. But, despite its growing presence in the ecstasy market and potential risks, crystal form has received little to no attention from an analytic or forensic perspective.

On the other hand, adulteration or replacement with other substances to increase economic gain, is common in illegal drugs such as ecstasy [2–4,11,12]. Although in most cases it is a matter of consumer fraud, there are some health related risks that must be taken into account as, for example, the low safety margins of adulterants such as 4-methylamine (4-MA), paramethoxyamphetamine (PMA), and paramethoxymethamphetamine (PMMA). These substances have been sold as MDMA or amphetamine and have also been associated to deaths in several European countries [13,14]. Health risks can be also related to purity, especially when users are unaware of the purity of the drugs they are consuming. This has been the case of ecstasy tablets with high doses of MDMA that can increase the risk of acute toxicity and of neurotoxic harm [15]. These issues, adulteration and purity, highlight the need to gather information about them regarding the crystal form of MDMA because no research has yet been conducted specifically on crystals and whether they differ from tablets.

In this paper, results of the analysis of 6200 drug specimens of ecstasy received in the Energy Control drug testing service over a period of 15 years are presented. Our objective is twofold: on the one hand, to present data about composition, purity and adulteration of MDMA sold in crystal form in the Spanish market and, on the other hand, to show the differences between crystals and tablets in relation to these two indicators. If these differences exist, they should be taken into account when researching ecstasy content in future research.

2. Method

2.1. Sample collection

Drug specimens collected between January 2000 and December 2014 were analyzed at Energy Control's facilities. This Spanish harm reduction project works with recreational drug users. Its drug testing service allows users to submit samples of their drugs to its headquarters to have their contents tested, and to obtain information and advice on risk reduction. Samples were also collected during outreach work in nightlife settings including electronic music festivals, clubs, and underground raves. Information regarding characteristics of the samples and tests results was included in an internal database.

2.2. Laboratory analysis

Sample identification was performed by a combination of validated analysis techniques. For the detection of substances and potentially toxic adulterants, two different chromatographic methods were used: thin layer chromatography (TLC) at the Energy Control headquarters, and gas chromatography coupled to mass spectrometry (GC/MS) at the IMIM-Hospital del Mar Medical Research Institute in Barcelona (IMIM). For TLC tests, TLC Silica gel 60 F254 (Ref: 1,05554,0001 from Merck) as stationary phase was employed. The TLC plate was developed with three different solvent systems: methanol/25% ammonia solution (100:2.5), methanol, and acetone. After development, analytes were identified comparing their position (retention factor) and colour in the Marquis test with a reference standard. The reference standards were supplied by IMIM.

To confirm TLC results, samples were reanalyzed by GC/MS. From 2000 to 2012 analyses were performed in an Agilent 5890 series II gas chromatograph coupled to a 5971A quadrupole mass spectrometer detector (Agilent). The gas chromatograph was fitted with a 6890 autosampler injector. Samples were injected in split mode into a 5% phenylmethylsilicone column (ULTRA-2, Agilent Technologies), 12 m × 0.2 mm i.d. and 0.33 μm film thickness. The oven temperature was initially maintained at 300 °C for 4 min, the total run time being 14.5 min. Insert liners packed with silanized glass wool were used. The injector and the interface were operated at 280 °C. Helium was used as carrier gas at a flow rate of 0.48 nl/min. The mass spectrometer was operated in electron impact ionization mode at 70 eV. GC/MS was run in scan mode. To identify the substance, retention time was used and to confirm the mass spectra two different libraries were used (2007 Wiley-VCH Verlag GmbH & Co. KgaA, Weinheim (Germany) reference library and SWGDRUG MS Library). From 2013 to 2014 ecstasy samples were analyzed using an Agilent 7890B gas Chromatograph coupled to a 5977A quadrupole mass spectrometer detector (Agilent; Santa Clara, CA, USA). The gas chromatograph was fitted with G4513A auto sampler injector. Samples were injected in split mode into a 30 m 0.25 mm i.d., 0.25 μm film thickness 5% phenylmethylsilicone column (HP-5MS, Agilent Technologies). The oven temperature was initially maintained at 90 °C for 2 min and programmed to reach 320 °C at 20 C per min. It was finally maintained at 320 °C for 9.5 min, the total run time was 21.5 min. Insert liners packed with silanized glasswool were used. The injector and the interface were operated at 280 °C. Helium was used as carrier gas at a flow rate of 1 mL/min. The mass spectrometer was operated in electron impact ionization mode at 70 eV. In order to confirm the mass spectra, four libraries were used: the Searchable Mass Spectral Library NIST/EPA/NIH Mass Spectral Library, Data Version: NIST 14; Searchable Mass Spectral Library Version 2.3 (http://www.swgdrug.org/ms.htm), Searchable Mass Spectral Library Cayman Spectral Library (CSL) (https://www.caymanchem.com/app/template/SpectralLibrary.vm) and the Energy Control's Mass Spectral library for internal use.

To determinine purity, ultraviolet spectrophotometry was performed in a Jenyway 6405 apparatus using extinction coefficients. Only unadulterated samples can be quantified by UV.

All statistical analyses were performed using the SPSS 15.0 statistical package.

3. Results

Between January 2000 and December 2014, 6200 samples purchased as ecstasy by their users were analyzed. The most frequent presentation of ecstasy was crystals (60.6%), particularly in the 8 last years evaluated, followed by tablets (38.8%) and, rarely, in other formats such as capsules, gels, paste, liquids, Vaseline, liquorice, and gum (0.6%). Crystals were mostly white whilst tablets varied in colour with different logos and shapes. Here, crystals include powders and crystal solids.

Four sample categories were defined in ecstasy specimens as a function of content: no psychoactive substance (NoPS), only MDMA, MDMA combined with one or more psychoactive