Forensic Science International 231 (2013) 88–91

Contents lists available at SciVerse ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Graphite furnace atomic absorption elemental analysis of ecstasy tablets

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ARTICLE INFO

Article history:
Received 3 December 2012
Received in revised form 4 April 2013
Accepted 17 April 2013
Available online 16 May 2013

Keywords:
MDMA
Ecstasy
Atomic absorption
Drug profiling

ABSTRACT

Six metals (copper, magnesium, barium, nickel, chromium and lead) were determined in two separate batches of seized ecstasy tablets by graphite furnace atomic absorption spectroscopy (GFAAS) following digestion with nitric acid and hydrogen peroxide. Large intra-batch variations were found as expected for tablets produced in clandestine laboratories. For example, nickel in batch 1 was present in the range 0.47–13.1 parts per million (ppm) and in batch 2 in the range 0.35–9.06 ppm. Although batch 1 had significantly higher 3,4-methylenedioxy-N-methamphetamine (MDMA) content than batch 2, barium was the only element which discriminated between the two ecstasy seizures (batch 1: 0.19–0.66 ppm, batch 2: 3.77–5.47 ppm).

1. Introduction

Classification of seized drugs by impurity profiling can provide useful forensic information to identify drug traffic routes, clandestine laboratories and methods of drug preparation [1]. Organic markers which originate from starting materials, intermediates, by-products and cutting agents can be determined by techniques such as high performance liquid chromatography (HPLC), gas chromatography-mass spectroscopy (GC–MS) [1] and more recently hydrophobic interaction liquid chromatography (HILIC) [2].

Elemental analysis is also used in drug profiling as it can give information about the catalysts used in synthesis, adulterants such as calcium carbonate and metal containers used during processing [1]. Techniques employed for inorganic impurity profiling studies have included flame atomic emission spectrometry (FAES) for cocaine [3]; flame atomic absorption spectrometry (FAAS) for cocaine [3] and methamphetamine [4]; graphite furnace atomic absorption spectrometry (GFAAS) for cocaine [3,5–7] and heroin [5–9]; inductively couple plasma-atomic emission spectrometry (ICP-AES) for 3,4-methylenedioxymethamphetamine (MDMA) [10,11] and heroin [8]; inductively couple plasma-mass spectroscopy (ICP-MS) for MDMA [10–12], methamphetamine [4,13] and heroin [14]; ion chromatography (IC) for methamphetamine [13]; total reflection X-ray fluorescence analysis (TXRF) for methamphetamines [15]; synchrotron radiation total reflection X-ray fluorescence analysis (SR-TXRF) for a range of drugs of abuse [16]; electrochemical methods for ecstasy [17].

MDMA has no legitimate medical uses and is the controlled substance in ecstasy tablets. Trace metals can be present in ecstasy tablets as a result of leaching of metal from reaction vessels, residues of catalysts and reducing agents, components of dyes and contaminants in the adulterants and cutting agents [18]. Although ICP-MS could be viewed as the method of choice due to its multi-element capabilities compared with FAAS and GFAAS and enhanced sensitivity compared with ICP-AES, it is still less commonly encountered in forensic laboratories than AAS techniques [19]. AAS systems are well established, cheaper to install and run, and require less user skill as well as less sample volume. GFAAS has not been previously reported with ecstasy tablets. This paper describes trace element analysis with GFAAS to determine the techniques ability to distinguish between two seized ecstasy batches.

2. Experimental

2.1. Reagents

Doubly distilled deionised water 18 mega-ohm (MΩ) water (Q system, Millipore Corp) was used throughout experimentation. Trace analysis grade chemicals were employed for the preparation of all solutions including the nitric acid (supplied by Sigma–Aldrich ≥69.0%, TraceSELECT) and hydrogen peroxide (supplied by Sigma–Aldrich ≥30%, TraceSELECT Ultra). All glassware and plastics were cleaned by soaking in diluted nitric acid (10%). Containers were then rinsed three times prior to use, with 18 MΩ water. The standard solutions of analytes used to perform the calibrations were prepared by diluting 1000 milligrams per litre (mg/L) stock

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http://dx.doi.org/10.1016/j.forsciint.2013.04.021

solutions of each analyte supplied by both PerkinElmer and Fischer Scientific with 18 MΩ water. The sample volume was 20 microlitres (μL), with the addition of 5 μL of 0.015 mg magnesium nitrate ($Mg(NO_3)_2$) matrix modifier (PerkinElmer) for the analysis of Cr as recommended by PerkinElmer. For the analysis of Pb 3 μL of 0.050 mg ammonium phosphate ($NH_4H_2PO_4$) (PerkinElmer) + 0.003 mg $Mg(NO_3)_2$ modifier was used.

2.2. Ecstasy samples

Two batches of ecstasy tablets were acquired from the TICTAC unit at St George's Hospital, Tooting, London, UK. HPLC analysis conducted at St. George's indicated that Batch 1 of 19 tablets contained significant quantities of MDMA while Batch 2 of 20 tablets contained predominantly caffeine.

2.3. Control samples

Copper mineral supplement tablets supplied by Swanson (Fargo, North Dakota, USA) were used as control samples. The tablets contained 2 mg copper as well as calcium carbonate, microcrystalline cellulose, stearic acid, magnesium stearate, croscarmellose sodium and food glaze.

2.4. Sample preparation

Samples were weighed in their tablet form before being crushed using a mortar and pestle and reweighed. The powder was then transferred to a 50 millilitre (mL) volumetric flask to which a mixture of 1 mL hydrogen peroxide and 5 mL nitric acid was added [11]. The solution was then placed in the sonicator for 10 min to aid the digestion and release any gas produced from the reaction before being placed into the oven for 1 h at 40 °C and 10 h at 90 °C under normal pressure. Samples were then transferred into 1.5 mL centrifuge tips and centrifuged at 1000 RPM for 5 min. The solution was decanted into a 15 mL Sarstedt centrifuge tube. 1 mL of 18 MΩ deionised water was added to the centrifuge tip and the sample was centrifuged at 1000 RPM for a further 5 min. The solution was decanted to the 15 mL Sarstedt centrifuge tube and filled to the 10 mL mark with 18 MΩ deionised water.

2.5. Instrumentation

GFAAS was performed using a PerkinElmer Analyst 800 atomic absorption spectrometer equipped with an AS-800 autosampler. A transversely-heated graphite furnace with stabilised temperature platform and a longitudinal Zeeman background corrector were used in all analyses. All lamps used were PerkinElmer hollow-cathode lamps. The system was operated via an integrated computer running AAWinlab32 software, version 3.4.0.0191. All elements were determined via graphite furnace atomic absorption spectroscopy, using argon as an inert gas.

3. Results and discussion

3.1. Selection of elements

The following elements were analysed: Cu, Mg, Ba, Ni, Cr and Pb. The selection of elements comprises of metals that may be present due to additives (Mg), dyes (Cu), reducing agents (Ni), catalysts and elements recorded to be commonly present in ecstasy tablets [4,10–12]. Elements Cu, Cr and Pb have been observed to be more homogenous within batches than elemental markers for synthesis routes [11] indicating these trace metals will be of use whilst indicating linkages between batches.

3.2. Detection limits and characteristic masses

The detection limit (based on three times the standard deviation of the blank) were calculated for each analyte examined. The detection limits for the elements determined on the graphite furnace AAS were found to be 0.1682 micrograms per litre (μg/L) for Cu, 0.0017 μg/L for Mg, 0.4357 μg/L for Ba, 1.5089 μg/L for Ni, 0.5068 μg/L for Cr and 0.2029 μg/L for Pb.

The characteristic masses (the mass of an analyte in picograms (pg) needed to produce an integrated peak area signal of 0.0044 absorbance-seconds) were determined on the graphite furnace AAS to be Cu: 16 pg, Mg: 1.6 pg, Ba: 33.9 pg, Ni: 17.9 pg, Cr: 3.4 pg and Pb: 43.0 pg.

Table 1
Control sample results.

Sample	Determined mass of Cu in tablet (mg)	Percentage recovery
Cu tablet 1	2.21	110
Cu tablet 2	1.96	98
Cu tablet 3	1.92	96
Mean (SD)	2.03 (0.16)	101 (7.6)

3.3. Sample preparation

To explore the repeatability and effectiveness of the digestion method three control samples were digested via the same procedure and then their copper content determined. Quantitative recoveries and percentage recoveries are displayed in Table 1.

As can be seen from Table 1 the mean mass determined (2.03 mg) was close to the nominal mass (2 mg) resulting in an average recovery of 101% with a percentage relative standard deviation (%RSD) of 7.6.

3.4. System performance

To ascertain the repeatability of the graphite furnace AAS system a known concentration of each element was analysed 10 times in one day, from this the %RSD was calculated for each element and is displayed in Table 2. For elements Cu, Ba, Ni, Cr and Pb a 10 ppb standard was analysed. For Mg a 5 ppb standard was analysed.

As can be seen from Table 2 the %RSD varies from element to element however they are all within 12%. Ba had the highest variation and this was observed throughout the study.

3.5. Determination of metals in ecstasy batches

For each tablet following digestion the concentration was determined via three replicates on three separate occasions resulting in a total of nine measurements per tablet. Results for batch 1 are given in Table 3 and those for batch 2 in Table 4.

The most striking aspect of the data is the large variation of the concentrations of some elements even within one batch, however this is not completely unexpected given previous studies of methamphetamine [4] and ecstasy tablets [10,11]. The copper levels in these samples are particularly high (batch 1: 4–2379 ppm, batch 2: 17–1851 ppm) compared with previous studies using ICP techniques which found ranges of 1–19 ppm [10] and 0.8–38 ppm [11] in ecstasy tablets.

In contrast the magnesium levels are significantly lower (batch 1: 3–180 ppm, batch 2: 3–8 ppm) where ranges of 86–4538 ppm [10] and 34–11,350 ppm [11] have been found previously suggesting significantly less magnesium stearate content in the current samples. The barium levels were relatively similar within each batch and were significantly higher in batch 2 (batch 1: 0.19–0.66 ppm, batch 2: 3.77–5.47 ppm). Barium was the only element that gave clear discrimination between the two batches as

Table 2
Repeatability results.

Element	Concentration (ppb)	%RSD
Ba	10	11.2
Pb	10	1.0
Cr	10	0.9
Ni	10	5.1
Cu	10	2.0
Mg	5	0.4