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Abstract: Six metals (Cu, Mg, Ba, Ni, Cr, Pb) 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 ppm and in batch 2 in the range 0.35-9.06 ppm. Although batch 1 had significantly higher 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).

Suggested Reviewers:

Graphite Furnace Atomic Absorption Elemental Analysis of Ecstasy Tablets

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Graphite Furnace Atomic Absorption Elemental Analysis of Ecstasy Tablets

Abstract

Six metals (Cu, Mg, Ba, Ni, Cr, Pb) 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 ppm and in batch 2 in the range 0.35-9.06 ppm. Although batch 1 had significantly higher 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).

Keywords: MDMA, ecstasy, atomic absorption, drug profiling.

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 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.

Experimental

Reagents

Doubly distilled deionised water (18 MΩ -Q system, Millipore Corp) was used throughout experimentation. Trace analysis grade chemicals were employed for the preparation of all solutions including the nitric acid and hydrogen peroxide. All glassware and plastics were cleaned by soaking in dilute nitric acid (10%) of trace analysis quality. 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 mg/L stock solutions of each analyte supplied by both Perkin Elmer and Fischer Scientific with 18 MΩ water. The sample volume was 20 µL, with the addition of 5µL of 0.015 mg $Mg(NO_3)_2$ matrix modifier for the analysis of Cr as recommended by Perkin Elmer. For the analysis of Pb 3µL of 0.050 mg $NH_4H_2PO_4$ + 0.003 mg $Mg(NO_3)_2$ modifier was used.

Ecstasy Samples

Two batches of ecstasy tablets were acquired from the TICTAC unit at St George's Hospital London Tooting. 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.

Control samples

Copper mineral supplement tablets supplied by Swanson 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.

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 mL volumetric flask to which a mixture of 1 mL 30% hydrogen peroxide and 5 mL 69% nitric acid was added [11]. The solution was then placed in the sonicator for 10 minutes to aid the digestion and release any gas produced from the reaction before being placed into the oven for 1 hour at 40 °C and 10 hours at 90°C under normal pressure. Samples were then transferred into 1.5 mL centrifuge tips and centrifuged at 1000 RPM for 5

minutes. 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 minutes. The solution was decanted to the 15 mL Sarstedt centrifuge tube and filled to the 10 mL mark with 18 MΩ deionised water.

Instrumentation

GFAAS was performed using a Perkin-Elmer 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 Perkin-Elmer 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.

Results and Discussion

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.

Detection Limits and Characteristic Masses

The detection limit (based on three times the standard deviation of the blank) and the characteristic masses (based on 0.0044 absorbance) were calculated for each analyte examined. The detection limits for the elements determined on the graphite furnace AAS were found to be 0.1682 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 for the elements determined on the graphite furnace AAS were found 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.

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.

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)

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 %RSD of 7.6.

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.

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

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.

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.

Table 3 Concentration (ppm) Metals in Samples from Batch 1

	Cu		Mg		Ba		Ni		Cr		Pb	
Samples	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
BATCH1.TAB1	2379	134	50.2	6.9	0.66	0.01	10.4	2.3	3.16	0.09	3.81	0.15
BATCH1.TAB2	9.8	1.1	17.5	1.4	0.44	0.02	13.1	2.4	1.59	0.07	0.17	0.04
BATCH1.TAB3	345	74	5.17	0.16	0.19	0.02	1.17	0.20	0.94	0.05	0.81	0.19
BATCH1.TAB4	338	73	5.81	0.15	0.62	0.06	1.46	0.15	1.82	0.11	0.72	0.08
BATCH1.TAB5	10.9	1.6	13.81	0.81	0.34	0.07	0.97	0.18	0.88	0.08	0.11	0.03
BATCH1.TAB6	172	18	5.93	0.12	0.35	0.02	2.20	0.37	1.82	0.13	0.48	0.12
BATCH1.TAB7	128	18	4.49	0.11	0.44	0.02	0.59	0.15	0.47	0.09	0.40	0.08
BATCH1.TAB8	4.26	0.32	11.10	0.20	0.39	0.01	4.95	1.27	1.28	0.06	0.16	0.03
BATCH1.TAB9	5.48	0.61	11.75	0.19	0.36	0.07	2.72	0.20	0.68	0.06	0.14	0.02
BATCH1.TAB10	8.03	0.76	10.51	0.36	0.28	0.06	0.95	0.13	0.87	0.01	0.11	0.02
BATCH1.TAB11	4.67	0.53	11.52	0.09	0.35	0.05	3.76	0.50	0.12	0.02	0.15	0.02
BATCH1.TAB12	83	13	3.25	0.04	0.28	0.05	0.84	0.14	0.31	0.04	0.40	0.06
BATCH1.TAB13	6.83	0.86	12.09	0.51	0.21	0.04	6.5	1.6	1.11	0.14	0.11	0.03
BATCH1.TAB14	33.1	2.0	13.68	0.41	0.31	0.04	0.47	0.14	0.19	0.04	0.17	0.04
BATCH1.TAB15	134	18	5.69	0.20	0.65	0.09	2.28	0.33	0.32	0.05	0.54	0.14
BATCH1.TAB16	74	12	180	25	0.21	0.02	2.29	0.28	1.65	0.27	0.28	0.07
BATCH1.TAB17	157	28	6.09	0.12	0.22	0.03	4.17	0.73	0.85	0.13	0.49	0.05
BATCH1.TAB18	15.07	0.26	14.27	0.51	0.25	0.03	1.51	0.31	0.73	0.11	0.16	0.02
BATCH1.TAB19	37.86	0.84	13.75	0.23	0.37	0.04	5.08	0.65	0.81	0.12	0.21	0.06

Table 4. Concentration (ppm) of Metals in Samples from Batch 2

	Cu		Mg		Ba		Ni		Cr		Pb	
Samples	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
BATCH2.TAB1	162	28	4.01	0.13	4.70	0.40	3.27	0.28	0.27	0.04	0.32	0.01
BATCH2.TAB2	23.55	0.46	8.66	0.06	5.07	0.67	0.82	0.11	0.34	0.07	0.13	0.02
BATCH2.TAB3	41.23	0.75	6.48	0.22	4.72	0.57	3.16	0.50	0.36	0.06	0.12	0.00
BATCH2.TAB4	131	26	5.23	0.15	4.40	0.53	0.97	0.17	0.32	0.08	0.25	0.00
BATCH2.TAB5	96	15	4.62	0.12	6.31	0.85	0.85	0.21	0.37	0.08	0.17	0.02
BATCH2.TAB6	101	23	5.95	0.17	5.24	0.68	0.84	0.13	0.23	0.07	0.20	0.01
BATCH2.TAB7	17.05	0.33	7.13	0.18	4.82	0.51	0.66	0.14	0.21	0.05	0.13	0.02
BATCH2.TAB8	240	45	3.86	0.11	5.30	0.76	0.67	0.10	0.27	0.04	0.54	0.13
BATCH2.TAB9	240	51	4.42	0.16	4.83	0.15	0.90	0.21	1.36	0.35	0.33	0.00
BATCH2.TAB10	88	20	3.22	0.08	3.77	0.42	0.35	0.09	0.12	0.01	0.22	0.00
BATCH2.TAB11	23.1	5.4	5.42	0.14	4.73	0.76	0.43	0.04	0.10	0.03	0.16	0.01
BATCH2.TAB12	1851	35	6.79	0.21	4.66	0.54	1.02	0.14	0.11	0.02	4.91	1.02
BATCH2.TAB13	54.11	0.41	8.35	0.15	5.10	0.30	2.30	0.29	0.23	0.04	0.16	0.00
BATCH2.TAB14	80	20	4.26	0.17	4.54	0.11	0.89	0.13	0.37	0.06	0.20	0.00
BATCH2.TAB15	67	16	3.48	0.14	4.92	1.09	1.93	0.27	0.31	0.05	0.12	0.02
BATCH2.TAB16	33.49	0.20	5.55	0.20	4.61	0.97	1.55	0.20	0.20	0.04	0.14	0.02
BATCH2.TAB17	118	23	6.23	0.22	4.61	0.61	1.67	0.27	0.18	0.03	0.25	0.02
BATCH2.TAB18	85	22	6.90	0.24	5.44	0.93	2.03	0.29	0.25	0.06	0.13	0.02
BATCH2.TAB19	71.37	0.63	4.56	0.21	5.47	1.00	7.10	0.77	0.28	0.06	0.13	0.01
BATCH2.TAB20	35.89	0.48	3.86	0.09	4.00	0.66	9.06	0.71	1.15	0.04	0.16	0.00

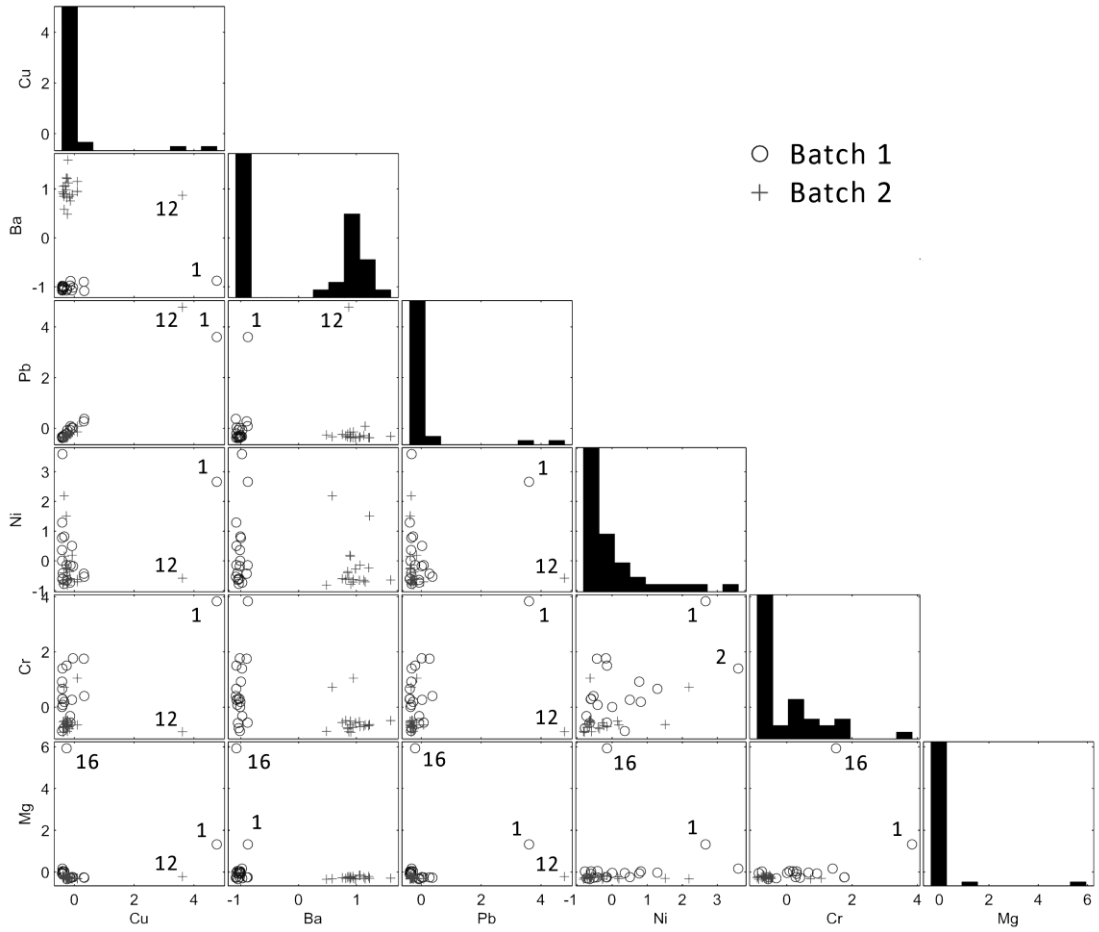
The most striking aspect of the data is the large variation of the concentrations of some elements even within one batch, however this is not completely unexpected given previous studies of methamphetamine [4] and ecstasy tablets [10,11]. The copper levels in these samples are particularly high (batch 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 illustrated in Figure 1 for which the data in Tables 3 and 4 was standardised prior to the creation of the array of pair-wise scatter plots. The levels found in batch 2 are very similar to the previously reported range of 3.6-6.0 ppm [11].

The ranges found for nickel (batch 1: 0.47-13.1 ppm, batch 2: 0.35-9.06 ppm) are very similar to previous reports of 1-25 ppm [10] and 0.3-16 ppm [11] while chromium levels (batch 1: 0.12-3.16 ppm, batch 2: 0.10-1.36 ppm) are lower than reported previously 0.7-34 ppm [11]. The range of lead concentrations (batch 1: 0.11-3.81 ppm, batch 2: 0.12-4.91 ppm) are similar to previously reported (0.02-10 ppm) [11]

Outliers are labelled in Figure 1. Tablet 2 from batch 1 and tablet 12 from batch 2 possess higher concentrations of Cu and Pb as can be seen from their separation from the group along the Cu axes or Pb axes. Tablet 1 from batch 1 also possesses a higher concentration of Cr as can be seen by the separation from the majority of the batch along the Cr axes. Tablets 1 and 16 from batch 1 possess higher concentrations of Mg. These outliers are due to the relatively inhomogenous nature of the tablet batches which may have resulted from poor premixing of powders prior to the tabletting process.

Figure 1 Pair-wise Scatter Plots. Outlying points are numbered.



Conclusions

Ecstasy samples were analysed for the first time via GFAAS determining the concentrations of 6 elements Cu, Mg, Ba, Ni, Cr and Pb. The results demonstrate acceptable detection limits and precision for seized drugs, hence quantifying trace metals in ecstasy tablets via GFAAS, which is more commonly available in forensic laboratories, can be considered as a viable technique for street drug analysis. As has been found previously, the ability of elemental analysis data to discriminate between batches of street tablets is limited by significant variation of metal concentrations present within each seizure [12]. Such variations will always be present in tablets produced in clandestine laboratories. In this study barium was the only element to offer discrimination between the two ecstasy seizures.

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