PRELIMINARY STUDIES IDENTIFYING AND QUANTIFYING TRACE METAL IMPURITIES IN ILLICIT ECSTASY TABLETS USING ATOMIC SPECTROMETRY TECHNIQUES

Ruth J. H. WADDELL, David LITTLEJOHN, Niamh NIC DAÉID
Forensic Science Unit, University of Strathclyde, Glasgow, United Kingdom

ABSTRACT: This paper illustrates some preliminary investigations into using ICP-MS in combination with ET-AAS in the analysis of Ecstasy tablets. Results indicate that a combination of both techniques can show discriminating power between seizures. Descriptions of the modifications made to optimise the ET-AAS system are described.

KEY WORDS: Ecstasy; ICP/MS, ET-AAS.

Problems of Forensic Sciences, vol. XLVII, 2001, 413–417
Received 23 February 2001; accepted 15 September 2001

INTRODUCTION

Ecstasy (3,4-methylenedioxymethylamphetamine or MDMA) is a member of the amphetamine drug class and, in the UK, is controlled under the Misuse of Drugs Act 1971 and the Misuse of Drugs Regulations 1985. Illegally synthesised in clandestine laboratories, Ecstasy is predominantly produced in tablet form, often with a distinctive motif. Profiling illicit drug seizures is essential in order to quantify the active constituent present and to gather drug intelligence. Quantification has ramifications in subsequent criminal proceedings while gathering intelligence may identify dealer-user networks. Currently, physical and chemical profiling relies on:

- physical description,
- presumptive tests,
- TLC;
- instrumental methods, generally chosen from HPLC, GC-FID, GC/MS or FT-IR.

Various synthetic routes are known for Ecstasy production, the chosen route often indicating the geographical origin of the seizure. In addition, route specific organic impurities are formed, which are identified by chromatographic methods, normally GCFID or GC/MS. The resulting chromatograms are known as "impurity profiles". Seizures with the same organic im-

purities may tentatively be linked to a common synthetic route although not necessarily to a common laboratory. However, where the same impurities are present in similar concentrations, the seizures may have originated from a common batch.

Elemental analysis of illicit seizures has the potential to augment organic impurity profiling, with the possibility of providing evidence to support both common route and batch links. Trace metals may be present in the seizure due to reducing agents/catalysts used during synthesis, leaching from vessels into the reaction mixture, contamination from diluents used to "bulk out" the tablets or external contamination, resulting from packaging and handling. In theory, seizures synthesised by the same route will contain common trace metals, which should be present in similar concentrations if the seizures originate from common laboratories. Potentially, such links may be enhanced where similar ratios of drug-bound versus unbound metal are determined.

In the literature, trace metal analysis of illicit heroin [3] and metamphetamine [2] seizures has been reported, using inductively coupled plasma-mass spectrometry (ICP/MS) and flame atomic absorption spectrometry (FAAS) for classification purposes. Little has been published for similar work involving Ecstasy seizures.

AIMS AND OBJECTIVES

The aim of this work is to investigate the possibility of initially detecting trace metal elements in illicit Ecstasy seizures by ICP/MS and quantifying selected metals using electrothermal atomic absorption spectrometry (ET-AAS). The initial objectives are:

1. To develop a reproducible method of sample preparation.
2. To rapidly screen illicit Ecstasy seizures using ICP/MS to identify elements of potential use in classification.
3. To obtain reproducible detection of Pb in illicit Ecstasy seizures with minimal interference effects, using ET-AAS.

EXPERIMENTAL METHODS

Sample preparation: Ecstasy tablets were powdered and digested (150 mg) in 10% HNO_3 , using a CEM 2000 microwave and following the digestion programme outlined in Table I. Digests were diluted to give a final concentration of 1.5 mg tablet/ml in 1% HNO_3.

A Sciex Elan 6000 ICP/MS instrument, set to the default parameters, was used to analyse the Ecstasy tablet digests. A UNICAM 929 ET-AAS Spectrometer was used to detect Pb in the tablet digests.

TABLE I. MICROWAVE DIGESTION PROGRAMME

Stage	1	2	3
Power [%]	60	60	60
Pressure [psi]	40	180	150
Time [min]	10	10	10
Time at pressure [min]	5	5	5

Using matrix-matched standards, linearity over the concentration range 0 to 30 ng Pb/ml was established and the regression equation and co-efficient of the calibration graph were determined. Digested tablets were analysed in triplicate and quantified, expressing the Pb concentration determined as μg Pb/g tablet in the original digest. In addition, a L'Vov platform was inserted into the furnace tube to investigate the benefits of platform atomisation over tube wall atomisation. The optimised furnace temperature programme for platform atomisation is presented in Table II.

TABLE II. OPTIMISED FURNACE TEMPERATURE PROGRAMME FOR PLATFORM ATOMISATION

Stage	Temp [°C]	Time [s]	Ramp [°C/s]	Gas type	Gas flow [ml/min]
Dry 1	80	20	10	Ar	200
Dry 2	150	40	2	Ar	200
Pyrolysis	700	30	50	Ar	200
Atomisation	2000	3	> 2000	Ar	0
Clean	2600	2	>2000	Ar	200

RESULTS AND DISCUSSION

Analysis by ICP/MS indicated significantly higher concentrations of Pb, Cu and Zn in the tablet digests compared with blank digests, as illustrated in Figure 1.

Pb was initially chosen for quantification by ET-AAS, due to its apparent ease of analysis. Using tube wall atomisation, there was poor recovery of Pb, especially at low concentrations (10 ng Pb/ml). However, with a L'Vov platform in place, improvements in recovery of up to 20% were obtained. For 4 different seizures, the calculated mean Pb concentrations ranged from 1.8 μg Pb/g tablet to 2.9 μg Pb/g tablet. Yet, despite platform atomisation, background absorbance was observed on the sample absorption profiles

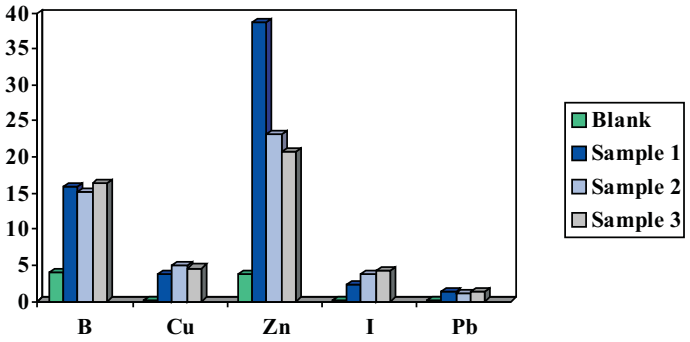

Fig. 1. Concentration of selected elements detected by ICP/MS.

Fig. 2a. 10 ng Pb/ml standard solution.

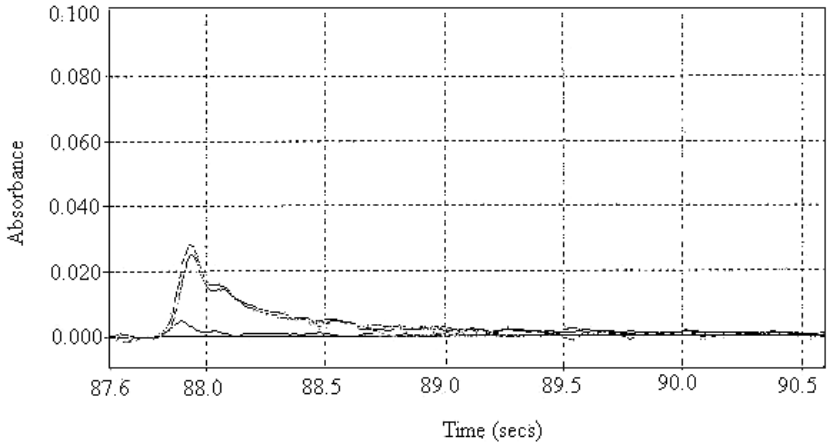

Fig. 2a. Sample NND 143 (1.5 mg/ml).

(Figure 2), indicating that the interference effect had not been fully eliminated. This was further supported with a spike and recovery experiment where Pb recoveries were found to be outwith the acceptable 95%–105% range [1].

CONCLUSIONS & FURTHER WORK

ICP/MS analysis proved to be effective in rapidly screening tablet digests to identify elements of potential use in chemical profiling. Additionally, ET-AAS analysis was successful in detecting low levels of Pb in acid digested Ecstasy tablets. However, in spite of platform atomisation, an interference effect continued to be present, as indicated by Pb recoveries which were outwith the acceptable 95%–105% range. The work has illustrated the potential benefits of trace metal analysis to enhance conventional profiling methods although the problem of interference effects remains to be fully addressed.

In terms of further work, numerous possibilities are available and, perhaps those of most interest include the analysis of a number of large Ecstasy seizures (which are known to be different from HPLC and GC/MS analysis) by ICP-MS to assess differences in the metals present and concentrations of each. To improve Pb recovery at low concentrations by ET-AAS and to investigate the use of alternative matrix modifiers such as palladium are also on interest. Quantification of the Pb concentration in a number of large Ecstasy seizures and, in combination with HPLC and GC-MS data, attempting to link seizures and expanding the ET-AAS technique for the detection of other trace metals indicated as potentially discriminating by ICP/MS analysis are being undertaken.

Acknowledgements:
Thanks to David Lyon for carrying out the ICP-MS analysis and also to the University of Strathclyde for providing financial assistance in funding this research.

References:

1. Lee M., Analytical method development in graphite furnace atomic absorption spectrometry, UNICAM Analytical Systems Furnace Course Manual.
2. Marumo Y., Inoue T., Seta S., Analysis of inorganic impurities in seized metamphetamine samples, *Forensic Science International* 1994, vol. 69, pp. 89–95.
3. Myors R., Wells R. J., Skopec S. V. [et al.], Preliminary investigation of heroin fingerprinting using trace element concentrations, *Analytical Communications* 1998, vol. 35, pp. 403–410.