

LETTER TO THE EDITORS

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Detection of amphetamines in fingernails: an alternative to hair analysis

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Abstract After external decontamination, the extraction of amphetamine (AP), 3,4-methylenedioxyamphetamine (MDA) and 3,4-methylenedioxymethamphetamine (MDMA) from hair and fingernails was accomplished via hot alkaline hydrolysis (1 ml 1 N NaOH, 10 min at 95 °C) in the presence of deuterated internal standards, followed by a three-step extraction procedure. The target drugs were derivatized by propionylation and analyzed by GC/MS operated in the electronic impact mode. Results indicated that AP, MDA and MDMA were present in both hair and fingernails. Their concentrations, slightly higher in fingernails than in head hair, were 10.2 and 12.0 ng/mg for AP, 8.0 and 9.7 ng/mg for MDA and 53.4 and 60.2 ng/mg for MDMA in head hair and in fingernails, respectively.

Key words Amphetamines · Hair · Fingernails · GC/MS

Introduction

A major limitation of blood and urine analyses is the relatively short retrospective time period for detecting drug exposure (Mieczkowski and Newel 1993). Therefore, hair analysis greatly expanded the time window for the detection of exposure to an illicit drug (Baumgartner et al. 1989) because it can reveal exposures from weeks to months prior to a test. It was reported that other keratin samples, e.g. nails, can accumulate drugs during chronic exposure (Miller et al. 1994). Only one paper reports a comparison between hair and nails and in 1994, Miller et al. demonstrated that the cocaine to benzoylecgonine ratio was approximately 5: 1 in hair and close to 1: 1 in nails. These authors also showed that the total concentrations of the target drugs in nail samples were substantially lower than those found in hair.

The following report describes a case where amphetamine (AP), 3,4-methylenedioxyamphetamine (MDA) and 3,4-methylenedioxymethamphetamine (MDMA) were simultaneously detected and quantified in head hair and in a fingernail.

Materials for examination

Head hair and one fingernail were obtained from a 22-year-old male known to be drug abuser. Hair samples were collected at the vertex posterior region, cut as close as possible to the skin, twice decontaminated in methylene chloride (5 ml, 2 min at room temperature) and pulverized in a ball mill. The fingernail was scraped with a scalpel and washed in methylene chloride.

Toxicological analyses

Hair (59 mg) and fingernail (14 mg) samples were incubated in 1 ml 1 N NaOH for 10 min at 95 °C in the presence of 200 ng deuterated internal standards (AP-, MA-, MDA- and MDMA-d₅, Radian, Austin, USA), according to our procedure (Kintz et al. 1995) for CNS stimulants.

After complete dissolution of the kerataneous matrix, the homogenate was extracted with 5 ml ethyl acetate, agitated (20 min at 95 cycles/min) and centrifuged (15 min at 3000 rpm). The organic phase was purified by 5 ml 0.2 N HCl and finally the drugs were backextracted in 5 ml ethyl acetate after alkalization with 2 ml 1 N NaOH. The organic phase was evaporated to dryness in the presence of 100 µl methanol: HCl (99: 1 v/v) to ensure non-volatility and derivatized with 50 µl pentafluoropropionic anhydride (PFPA) + 35 µl 2,2,3,3,3-pentafluoro-1-propanol (PFP-OH) (Aldrich, Gillingham, UK).

The derivatized extract was evaporated under a stream of nitrogen, dissolved in 30 µl of ethyl acetate and injected through the column (HP-5MS capillary column, 5% phenyl-95% methylsiloxane, 30 m × 0.25 mm i.d.) of a Hewlett Packard GC/MS system (5890 gas chromatograph coupled with a 5989 B mass detector). Injector temperature

Table 1 AP and MDA concentrations ($\mu\text{g/l}$) in urine and blood samples

Concn ($\mu\text{g/l}$)	AP	MDA
Urine	251	781
Blood	7.1	151

was 240 °C and splitless injection was employed with a split-valve off-time of 1.0 min. The flow of carrier gas through the column was 1.0 ml/min (helium, purity grade N55). The column oven temperature was programmed to rise from an initial temperature of 70 °C (kept for 2 min) to 280 °C (kept for the final 6 min) at 20 °C/min.

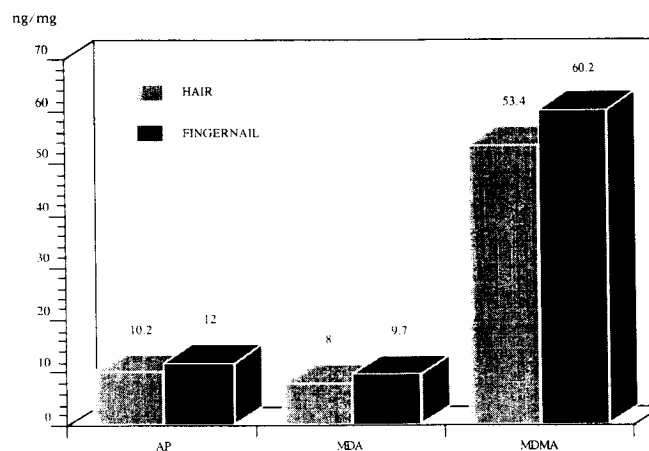
The detector was used in electronic impact mode at 70 eV with an ion source temperature of 250 °C. The electron multiplier voltage was set at +400 V above the autotune voltage.

Qualitative and quantitative analyses were obtained in single ion monitoring mode by comparison of retention times and relative abundance of three confirming ions to the IS-ds.

Results and discussion

AP and MDA tested positive in both urine and blood samples. Concentrations are presented in Table 1. MA and MDMA were not detected. Therefore, hair and fingernail samples were tested for the investigation of chronic drug abuse. The results are summarized in the Fig. 1.

These results indicate that AP, MAD and MDMA were abused for a long time before the test. The preliminary results obtained with urine and blood samples did not reveal the chronic consumption of MDMA that is demonstrated by the high concentration (53.4 ng/ml) found in head hair. The results obtained after investigation of the fingernail sample are in accordance with those obtained with hair analysis and the concentrations determined were slightly higher than those obtained in hair samples. We found 10.2 and 12.0 ng/mg for AP, 8.0 and 9.7 ng/mg for MDA and 53.4 and 60.2

**Fig. 1** AP, MDA and MDMA concentrations (ng/mg) in hair and fingernail samples

60.2 ng/mg for MDMA in head hair and in fingernails, respectively. This observation is not in accordance with the data of Miller et al. (1994) where concentrations in the hair were largely higher than those in nails.

More extensive research appears to be necessary to validate our findings.

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