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EUROPEAN PROJECT RESPONSE to challenges in forensic drugs analyses

HEROIN PROFILING – methodology development and first impressions

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INTRODUCTION

Profiling of heroin samples for study trafficking and distribution networks is commonly performed by dealing with the characterization of main heroin alkaloids, e.g. diacetylmorphine, meconin, acetylcodeine, acetylthebaol, 6-monoacetylmorphine, papaverine, and noscapine. Several GC methods with derivatization to avoid problems associated with transacetylation were already developed, mostly by using flame ionization detector.

In National Forensic Laboratory we used GC-MS method for heroin profiling. The heroin samples were derivatized with MSTFA prior the analysis. The specific target and qualifier ions were selected for the main heroin alkaloids to measure the area of the peaks.

For successful assessment of links between heroin samples with different diacetylmorphine concentration, samples were prepared by weighing homogenized powder containing approximately 1,2 mg of diacetylmorphine base, which is equivalent for 15 mg of 8% heroin concentration. The concentration threshold above 8% was established through validation of the GC MS method. We observed non-linear behavior of GC-MS method, which was not mentioned in previous studies of heroin profiling methods.

Similarity (dissimilarity) among samples was evaluated by multivariate analysis using Pearson correlation. To achieve similar magnitude of target variables for Pearson correlation, each area of main heroin alkaloids was pretreated with a standard deviation, calculated from areas of particular alkaloid through long-term measurements.

To evaluate the discriminative power of the method the distribution of inter and intra variability was investigated.

Intravariability distribution was evaluated by measuring over a longer period the similarity value (in our case the Pearson correlation) between pairs of samples from the same seizure 100 measurements have been calculated for evaluating the intravariability of heroin.

Intervariability was evaluated by measuring Pearson value between pairs of samples selected from different seizures in the period from 2014 to 2015. 70 real samples from 70 different seizures were analyzed.

We determined the thresholds for linked and non-linked samples.

Sample preparation

An amount of homogenized sample equivalent to 1,2 mg of diacetylmorphine base was weighed and dissolved in 1 mL of chloroform/pyridine mixture (5:1), followed by adding 100 µL of MSTFA with 1% TMCS, and heated for 2 hours at 80°C.

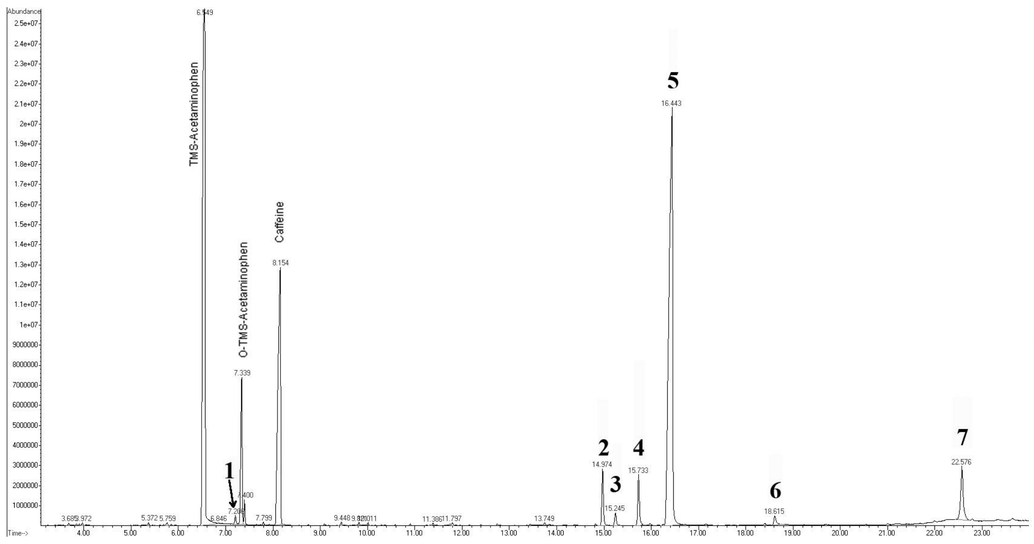

FIGURE 1: Typical chromatogram of derivatized heroin with main alkaloids and impurities. Peaks: (1) meconin (MEC), (2) acetycodeine (COD), (3) acetythebaol (THEB), (4) TMS—6-monoacetymorphine (6-MAM), (5) diacetymorphine (DAM) , (6) papaverine (PAP), and (7) noscapine (NOS). Tepmerature program was: initial temperature 150 °C for 1 min, 10 °C/min to 250 °C (0 min), then 4 °C/min to 290 °C (0 min), 30 °C/min to final temperature 300 °C (2 min).. The injector and detector temperatures were set 290 and 280 °C respectively.

Pearson correlation

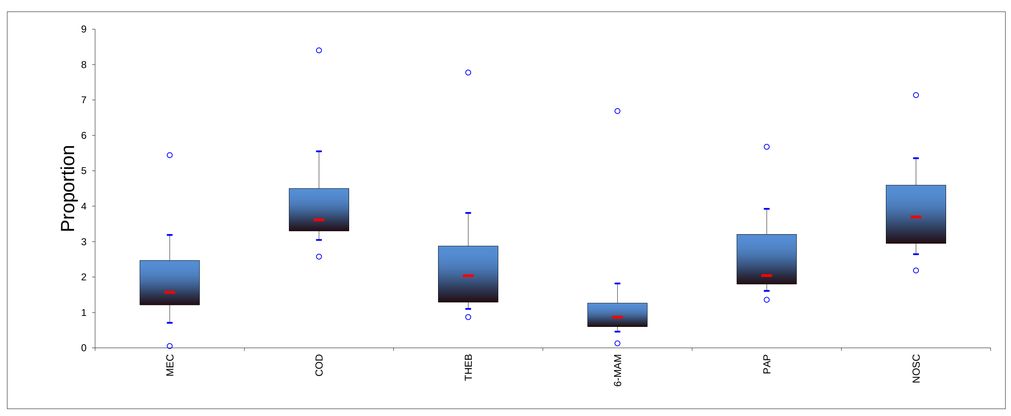

FIGURE 3: Representation of the proportion of each target compounds after data pretreatment.

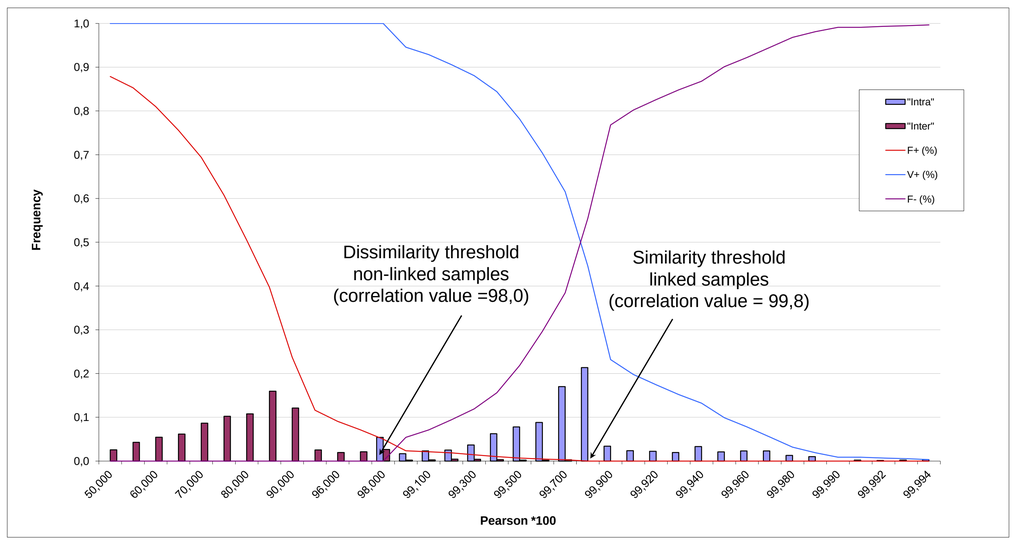

FIGURE 4: Distribution of the correlation scores for linked (intra) and non-linked (inter) heroin samples.

Gas chromatographic analysis

GC	Agilent 7890B
MS detector	Agilent 5977A
liner	deactivated glass wool
Column	Agilent HP-1 MS column
Carrier gas	He (constant flow 0.9 ml/min)
injection volume	2 µL
split mode	1:50

Typical chromatogram corresponding to the method is shown in **Figure 1.**

Limitation of the GC MS method

The concentration threshold above 8% was established through validation of the GC-MS method. We observed non-linear behavior of GC-MS method, which was not mentioned in previous studies of heroin profiling methods. Non-linear behavior is shown in **Figure 2.**

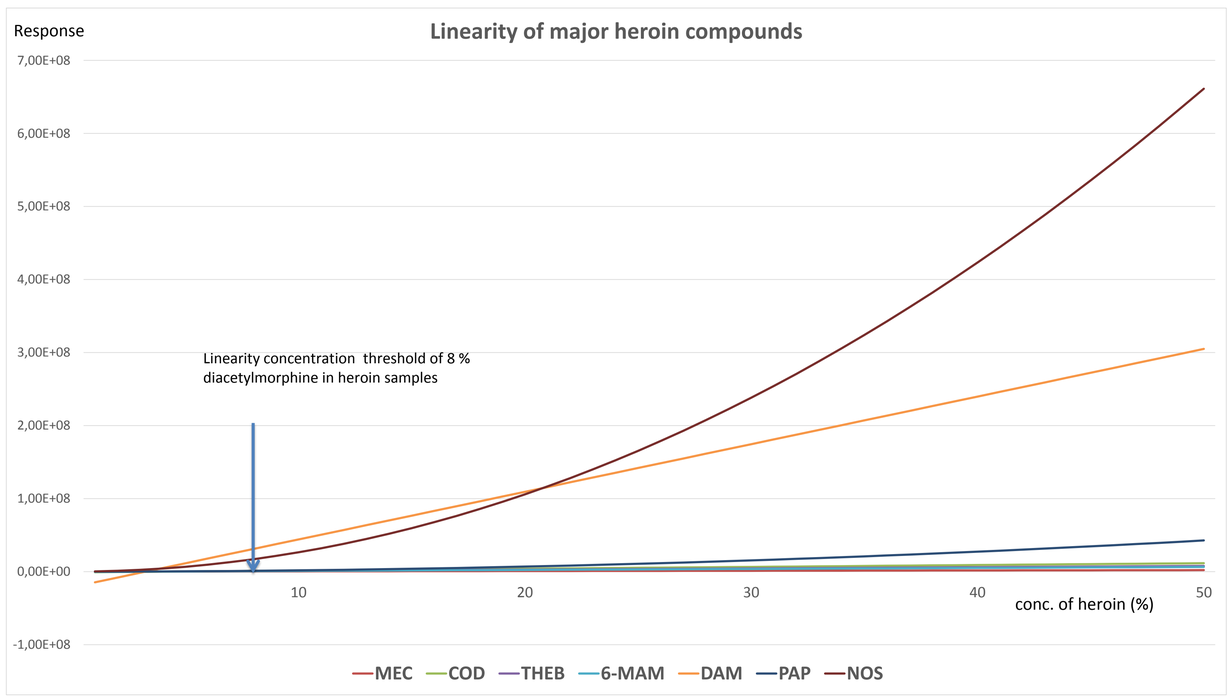

FIGURE 2: Graphical presentations of non-linear behavior for target compounds analyzed by GC -MS.

First impressions

Police seized 9 heroin samples (A, B, C, D, E, F, G, H, I) at different time period and asked for comparison.

By GC-MS analysis, we found
- All samples contained paracetamol and caffeine.
- The diacetylmorphine concentration in all samples was in the range from 10 to 15 % for all samples.

no significant differences between samples

By GC-MS heroin profiling method, we found
- A, B, E samples were neither linked to each other nor to the any other sample.
- C, D, F, G samples were linked to each other, but not to the any other sample.
- H, I samples were linked to each other, but not linked to the any other sample.

significant differences between samples

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