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, acetyloscodeine, acetylthebaol, 6-monoacetylmorphine, papaverine, and noscapine. Several GC methods with derivatization to avoid problems associated with transacylation 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.

To evaluate the discriminative power of the method the distribution of inter and intra variability was investigated. Intervariability 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 distribution 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) acetyloscodeine (COD), (3) acetylated thebaol (THEB), (4) TMS-6-monooacetylmorphine (6-MAM), (5) diacetylmorphine (DAM), (6) papaverine (PAP), and (7) noscapine (NOS). Temperature 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.

Gas chromatographic analysis

<table>
<thead>
<tr>
<th>GC</th>
<th>Agilent 7890B</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS detector</td>
<td>Agilent 5977A</td>
</tr>
<tr>
<td>Liner</td>
<td>deactivated glass wool</td>
</tr>
<tr>
<td>Column</td>
<td>Agilent HP-1 MS column</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>He (constant flow 0.9 ml/min)</td>
</tr>
<tr>
<td>Injection volume</td>
<td>2 µL</td>
</tr>
<tr>
<td>Split mode</td>
<td>1:50</td>
</tr>
</tbody>
</table>

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.

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.
- 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.

This work has been produced with the financial support of the Prevention of and fight against crime Programme of the European Union (grant agreement number 222613 – SEC/DRUG/AS/6/4413). The contents of this publication are the sole responsibility of the authors and can in no way be taken to reflect the views of the European Commission.

Co-funded by the Prevention of and Fight against Crime Programme of the European Union.

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

22nd ENFSI-DWS meeting, May 10th-12th 2016, Bled, Slovenia