Forensic Science International 207 (2011) 27–34

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Illicit drug profiling, reflection on statistical comparisons

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ARTICLE INFO

Article history:
Received 30 November 2009
Received in revised form 17 August 2010
Accepted 23 August 2010
Available online 25 September 2010

Keywords:
Drug profiling
Heroin
Cocaine
Statistical treatment

ABSTRACT

This paper presents reflexions about statistical considerations on illicit drug profiling and more specifically about the calculation of threshold for determining of the seizure are linked or not. The specific case of heroin and cocaine profiling is presented with the necessary details on the target profiling variables (major alkaloids) selected and the analytical method used. Statistical approach to compare illicit drug seizures is also presented with the introduction of different scenarios dealing with different data pre-treatment or transformation of variables.

The main aim consists to demonstrate the influence of data pre-treatment on the statistical outputs. A thorough study of the evolution of the true positive rate (TP) and the false positive rate (FP) in heroin and cocaine comparison is then proposed to investigate this specific topic and to demonstrate that there is no universal approach available and that the calculations have to be revaluate for each new specific application.

1. Introduction

This paper presents important results regarding statistical data treatment and more specifically the problematic of data pre-treatment in the comparison of illicit drug samples for profiling purpose. The literature proposes various approaches for comparing illicit drugs samples when dealing with large database mainly using similarity measurement like distance (e.g. Euclidian distance) or correlation measurement [1–10].

Measuring these distances or correlations is not of major difficulty whereas the understanding and the interpretation of these values are not a trivial aspect. Correlations and distances measurements involve the use of threshold's notion. Experts want to delimit a value acting as a decision-maker for determining if the samples are linked or not. We will demonstrate that these thresholds are not fixed values but that they depend among other things on the analytical method used, the data handling of the target variables (ranking and transformation like normalization, square root transformation or linear transformation) as well as the selected strategies (e.g. operational vs. evidential purposes).

This crucial point will be investigated using different scenarios for heroin and cocaine profiling. The main aim consists to demonstrate the necessity of evaluating in detail the discriminative power of each scenario in order to draw a conclusion.

The remainder of the paper is organized as follows. Section 2 describes the samples used for the research as well as the target variables. Section 3 presents the analytical methods used to extract the chemical profiles. Then, Section 4 describes the different scenarios proposed in this study to test the statistical methods. Section 5 presents the results and the discussions with regards to the different selected scenarios. Finally, the last section highlights the main results and suggests areas for futures work.

2. Sampling and target compounds

The data set used for the statistical treatment compiles heroin and cocaine samples analysed during the last 3 years (2007–2009). The analysis have been done on 144 heroin seizures and 232 cocaine seizures representing, respectively 764 heroin samples and 1693 cocaine samples.

The target compounds selected for heroin samples are: meconine, acetylcodeine, acetylthebaol, 6-monoacetylmorphine, diamorphine (heroin), papaverine and noscapine. The following cutting agent have also been identified and included in the method: phenacetin, paracetamol, fructose, caffeine, glucose, mannitol, gluconic acid, inositol, lactose, sucrose and griseofulvin.

The following compounds are extracted in the cocaine samples: ecgonine, ecgonine methylester, tropacocaine, benzoylecgonine, norcocaine, cocaine, cis-cinnamoylcocaine, trans-cinnamoylcocaine, trimethoxycocaine. The main cutting agent encountered in cocaine seizures have also been identified and included in the method: malic acid, nicotinamide, methylephedrin, 1-4 dimethylterephtalate, acetylsalicylate, creatinin, ephedrin, diethyl phthalate, phenacetin, phenylalanin, paracetamol, lidocain, benzocain, glycerol 3-phosphate, metformin, caffeine, fructose, citric acid, glucose, theophyllin, mannitol, sorbitol, dulcitol, ascorbic acid,

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doi:10.1016/j.forsciint.2010.08.015

Table 1
List of the targeted ions for each compound extracted for the determination of the chemical signature of heroin samples as well as for the main cutting agent.

Heroin samples	Peak no.	RRT	Target	Qualifiers
Heneicosane (internal standard)		1.000 (RT 10.606)	57	71, 85
Meconine (MEC)	1	0.613	194	165
Acetylcodeine (COD)	2	1.468	341	282, 229
Acetylthebaol (THEB)	3	1.465	254	239
6-Monoacetylmorphine (MAM)	4	1.509	399	340, 287
Diamorphine (DAM)	5	1.595	369	327, 268
Papaverine (PAP)	6	1.777	338	324
Noscapine (NOSC)	7	2.143	220	205
Phenacetin		0.470	236	251, 222, 162
Paracetamol		0.500	295	280, 206
Fructose		0.702	217	437, 257
Caffeine		0.715	194	109
Glucose		0.799	204	217, 231, 191
Mannitol		0.780	319	421, 345, 305
Gluconic acid		0.924	292	333, 359
Inositol		1.015	305	318, 191, 265
Lactose		1.495	204	361, 217, 191
Sucrose		1.596	361	437, 271, 217
Griseofulvin		1.712	352	321, 310, 284

levamisol, glucoronic acid, inositol, procain, tetracain, diazepam, dioctyl phtalate, sucrose, lactose, maltose, hydroxyzin, diltiazem.

Standard have been purchase from Lipomed AG and SIGMA® for the cutting agent except from meconine, acetylthebaol and trimethoxycocaine that have been identified by custom and commercial library as well as literature references.

3. Analytical method and validation

Since 2006, the profiling procedure has been moved from GC-FID to GC–MS method. This migration has been motivated by the results obtained in different profiling research [11,12] demonstrating that GC–MS technology offers analytical performance (repeatability, linearity, stability, reproducibility, resolving power, sensibility,...) comparable or even better than GC-FID and also becomes a method of choice for the illicit drug profiling. Furthermore, the "target ion" quantification functionality (the target compounds in the MS chromatograms were quantified with one specific ion for each substance) is also another aspect promoting GC–MS mainly for avoiding the problematic of co-elution of compounds and for increasing the quality of target compounds quantification. It also has the advantage to permit a quantification of the main compounds (DAM and cocaine) in the same run.

The heroin and cocaine samples were prepared by weighing approximately 8 mg of the homogenised powder. The analysis is done in triplicate. The samples are then dissolved in a 500 μl solution of $CHCl_3$/pyridine 5:1 and 100 μl of MSTFA. This solution is then heated at 80 °C in an air oven for 1 h.

The analyses were separate on a HP-5MS column (30 m × 0.25 mm, d_f 0.25 μm) for cocaine samples and on a DB5-MS (30 m × 0.25 mm, d_f 0.25 μm) for heroin samples. The injection is made in a split mode with a general purpose split liner (vol. 870 μl, Agilent Technologies No. 5183-4711 4 mm ID) packed with glass wool. 2 μl of the sample is injected at 230 °C for the cocaine sample and at 250 °C for heroin sample with a total gas flow of 53.8 ml/min for heroin and 24.1 ml/min for cocaine and a split ratio of 1:20 for cocaine (gas saver 15 ml/min after 2 min) and 1:50 for heroin (gas saver 20 ml/min after 2 min). Helium is use as carrier gas with a constant flow mode (1 ml/min) (see Fig. 1 for a typical heroin' chromatogram and Fig. 2 for cocaine).

For cocaine samples, the temperature program starts at 180 °C (1 min) and then increases to 275 °C (4 °C/min) and holds for 5.25 min for a total run of 30 min. For heroin samples, the temperature program starts at 150 °C and then increases to 250 °C (8 °C/min) and then to 320 °C (6 °C/min) for a total run of 24.17 min.

Table 2
List of the targeted ions for each compound extracted for the determination of the chemical signature of cocaine samples as well as for the main cutting agent.

Cocaine samples	Peak no.	RRT	Target	Qualifiers
Heneicosane (internal standard)		1.000 (RT 9.303)	57	71, 85
Ecgonine methylester (EME)	1	0.340	82	96, 147
Ecgonine (EC)	2	0.402	82	96, 182
Tropacocaine (TROPA)	3	0.812	124	245, 82
Cocaine (COC)	4	1.299	182	82, 303
Benzoylecgonine (BENZO)	5	1.410	240	82, 105
Norcocaine (NOR)	6	1.442	240	105
Cis-cinnamoylcocaine (CIS)	7	1.651	182	82, 96
Trans-cinnamoylcocaine (TRANS)	8	1.915	182	82, 131
Trimethoxycocaine (TRIME)	9	2.445	182	393, 94
Malic acid		0.349	233	245, 335, 190
Nicotinamide		0.300	179	136, 193
Methylephedrin		0.312	72	163, 102
1-4 Dimethylterephtalate		0.289	163	194, 135
Acetylsalicylate		0.329	195	210, 177, 135
Creatinin		0.353	115	171, 329
Ephedrin		0.353	130	147, 294
Diethyl phthalate		0.471	149	177, 105
Phenacetin		0.353	236	251, 162
Phenylalanin		0.450	218	192, 266, 100
Paracetamol		0.373	206	280, 295
Lidocain		0.503	86	220, 235
Benzocain		0.544	237	222, 192, 149
Glycerol 3-phosphate		0.579	357	299, 445, 315
Metformin		0.612	299	284, 256, 171
Caffeine		0.618	194	109
Fructose		0.720	437	217, 191
Citric acid		0.584	273	363, 347, 305
Glucose		0.702	204	305, 129, 103
Theophyllin		0.801	237	252, 223, 178
Mannitol		0.768	319	205, 103
Sorbitol		0.768	319	217, 205, 189
Dulcitol		0.768	319	217, 307
Ascorbic acid		0.801	332	205, 117
Levamisol		0.843	148	204, 101
Glucoronic acid		0.991	333	292, 359, 423
Inositol		1.060	305	265, 217, 191
Procain		1.311	99	182, 272
Tetracain		1.435	193	176, 150
Diazepam		1.891	283	256, 221, 165
Dioctyl phtalate		2.013	149	167, 279
Sucrose		2.320	437	217, 271
Lactose		2.187	361	521, 243
Maltose		2.423	204	405, 315, 243
Hydro xyzin		2.710	201	299
Diltiazem		2.740	58	71, 207

The mass spectrometer was operated with a solvent delay of 2 min. The scanning range was 30–450 amu, with a sampling rate of 1.77 scans/s for heroin and 30–550 amu with a sampling rate of 1.44 scans/s for cocaine. The temperature of the transfer line, the ion source and the quadrupole of the MS were set up at 250 for cocaine and 280 for heroin, 230 and 150 °C, respectively. The method was also able to identify the most common cutting agent of heroin and cocaine samples.

The target and qualifiers ions selected for the main alkaloids and the most common cutting agent are listed in Tables 1 and 2.

For the validation aspect of these 2 methods, the profiling context has been considered. Taking into consideration that we are working with database, it is compulsory that the precision (repeatability and intermediate precision) was achieved for all compounds considered in the profile. Repeatability was expressed as the coefficient of variation (CV) of the intra-day analysis of