Case report

Drug Testing and Analysis

Received: 30 January 2012 Revised: 10 February 2012 Accepted: 10 February 2012

(www.drugtestinganalysis.com) DOI 10.1002/dta.1335

A rapid method for profiling samples of illicit heroin

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The aim of this investigation was to profile samples of illicit heroin. It involved derivatization and gas chromatographic separation followed by a fully automated data analysis. Six major constituents (acetylcodeine, 6-monoacetylmorphine, papaverine, noscapine, codeine, and morphine) were tested and analyzed. The square cosine function was used to evaluate correlation values. The method proved to be efficient and reliable providing information on links between illicit heroin samples. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: heroin; gas chromatography; cosine function; correlation values

Introduction

The presence of different additives/compounds in illicit drugs can be used to characterize the link or common origin of illegal samples,[1–4] which contributes important information for legal and intelligence purposes. A variety of analytical techniques has been described in the literature among which gas chromatography (GC) has been the preferred method, enabling an adequate resolution concerning impurity separation together with appropriate sensitivity and reproducibility. Most of the methods need professional skills to perform the extraction, centrifugation, and evaporation and involve a rather long preparation.[5–8] Esseiva[9] developed a new method focusing on the main impurities of illicit drugs, requiring modest sample preparation efforts. The cosine function was used to calculate the correlation values of illicit heroin samples, which gave a single numerical value rather than a graphical representation (e.g. the dendrogram from a cluster analysis).

In China, confiscated heroin samples mainly originate from south-east Asia. Its chemical profile is not the same as eastern Europe's (which originates mainly from south-west Asia).[10] So we would build a similar method for prospecting intelligence.

Materials and methods

Reagents and chemicals

Anhydrous acetonitrile and pyridine were of analytical grade, purchased from Beijing Chemical Reagent Ltd (Beijing, China). The internal standard (n-alkane, C20) was obtained from Fluka (Milwaukee, WI, USA). MSTFA (*N*-methyl-*N*-trimethylsilyltrifluoroacetamide) was bought from Acros (Morris Plains, NJ, USA). All powder from samples discussed in this paper were obtained from street seizures, which were confiscated by the Beijing, Tianjin, Shijiazhuang, and Chengtu police in 2007 and 2008. Heroin, morphine, 6-monoacetylmorphine, codeine, acetylcodeine, papaverine, and noscapine standards were sourced from the National Narcotics Laboratory (Beijing, China).

Sample preparation

About 1 g of heroin sample was homogenized in an agate mortar. Eight milligrams of the sample were weighed and transferred into a glass vial. The sample was dissolved in 1.2-ml acetonitrile/pyridine mixture (5:1) with 1 mg/ml of internal standard (C20) and then 100 μl of MSTFA was added. The sample was incubated for 40 min at 80°C and injected into the GC.

GC conditions

An Agilent 6890 gas chromatograph equipped with a flame ionization detector (GC-FID) was used with chromatographic separation achieved on a DB-5 capillary column (length 30 m, i.d. 0.32 mm, film thickness 0.25 μm, Agilent) with helium as carrier gas at a pressure of 151.7 kPa (flow =1.43 ml/min). The injection temperature was maintained at 290°C; the detector temperature at 325°C; the injection volume 2 μl; and the split ratio 17:1. The oven temperature was programmed as follows: initial temperature was 150°C held for 1 min, followed by an increase of 8°C/min to 250°C, and then an increase of 6°C/min to 320°C (held for 1 min).

Data analysis

For each heroin sample, a chromatographic profile was obtained by GC-FID. The quantities of six target compounds (acetylcodeine, 6-monoacetylmorphine, papaverine, noscapine, codeine, and morphine) and diacetylmorphine were obtained on the GC-FID. Processing of peak areas were performed in GC Chemstation (Agilent Technologies Co.) and Excel 2003 (Microsoft Co.). Each peak area was calculated relative to C20. Then normalization was

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performed with the diacetylmorphine. The chemical data were transferred to a database, along with other relevant investigation results and chemical information including seizure details, arresting officer's details, number of samples in the seizure, purity, and cutting agents. The correlation value was performed with SPSS 16.0.

The method would outline any similarity between two samples using the cosine function.[9–12] The angle between two vectors was:

$$\cos^2\theta = \frac{\left(\vec{a}\cdot\vec{b}\right)^2}{\left\|\vec{a}\right\|^2 \times \left\|\vec{b}\right\|^2} = \frac{(a_1b_1 + a_2b_2 + \ldots + a_nb_n)^2}{\left(a_1^2 + a_2^2 + \ldots + a_n^2\right) \times \left(b_1^2 + b_2^2 + \ldots + b_n^2\right)} \qquad (1)$$

The correlation value, C, between two chromatograms was given by:

$$C = 100 \times \cos^2\theta = 100 \times \left[\frac{(a_1b_1 + a_2b_2 + \ldots + a_nb_n)^2}{\left(a_1^2 + a_2^2 + \ldots + a_n^2\right) \times \left(b_1^2 + b_2^2 + \ldots + b_n^2\right)}\right] \qquad (2)$$

where $a_1, a_2, \ldots, a_n$ represented the values of the variables 1-n for chromatogram a, and $b_1, b_2, \ldots, b_n$ represented the values of the variables 1-n for chromatogram b.

Results and discussion

Purity of street heroin samples

A total of 119 non-linked samples were obtained randomly from various non-linked seizures, and each seizure corresponded to one sample. The purity of heroin samples ranged typically from 5% to 80% (109/119) with 38% (45/119) of the samples comprising heroin between 10% and 20% only (Figure 1).

Target compounds selection

The method was first developed in Switzerland and it was necessary to check if Chinese samples were comparable to the Swiss materials that necessitated the analysis of six target compounds: meconin, papaverine, noscapine, acetylcodeine, 6-monoacetylmorphine, and acetyltebaol.[9]

However, meconin and acetyltebaol were not present in almost any Chinese samples. Fortunately, codeine and morphine were present in most of the chromatograms together with four impurities (acetylcodeine, 6-monoacetylmorphine, papaverine, and noscapine). A typical chromatogram is shown in Figure 2.

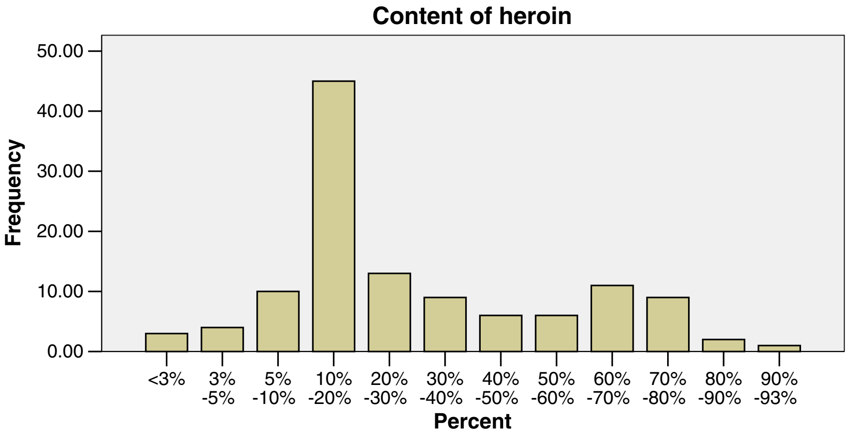

Figure 1. The distribution of purity of street heroin samples.

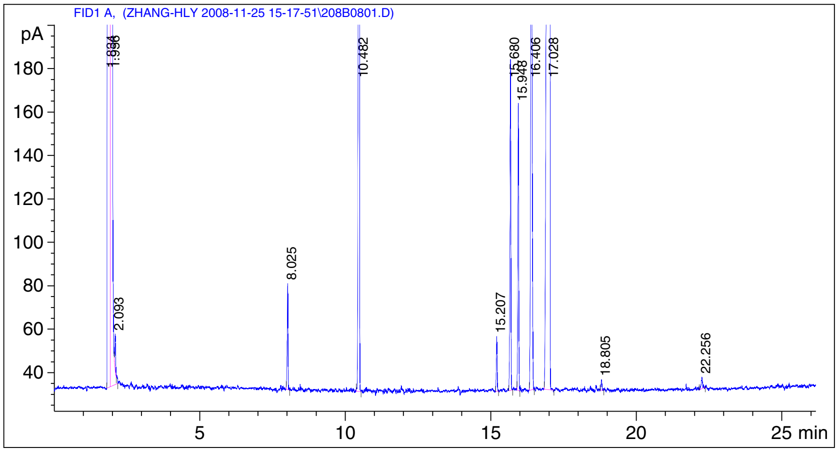

Figure 2. Typical chromatogram of heroin major impurities. The relative retention time of 10.482 15.207 15.680 15.948 16.406 17.028 18.805 22.256 was internal standard, codeine, acetylcodeine, morphine, 6-monoacetylmorphine, heroin, papaverine, and noscapine, respectively.

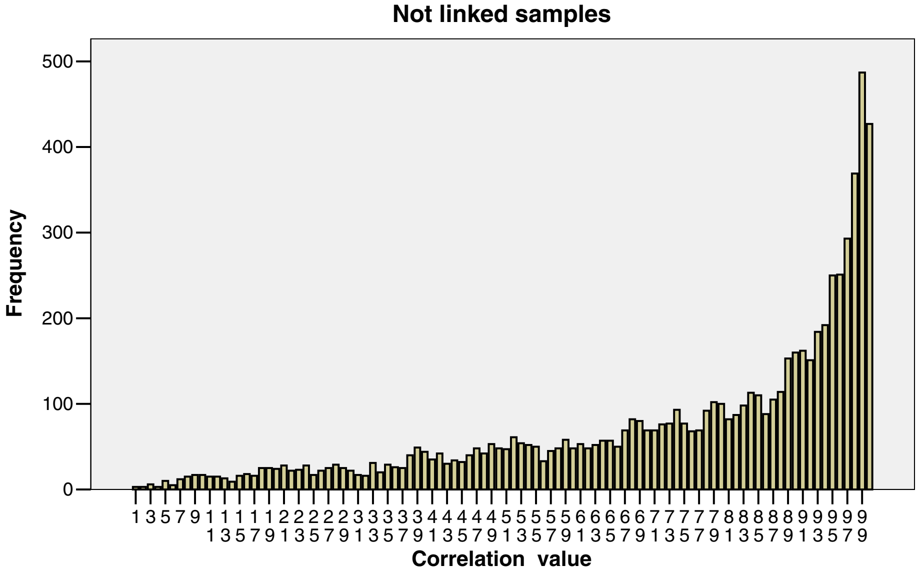

Figure 3. Distribution of correlation values of non-linked 119 samples.

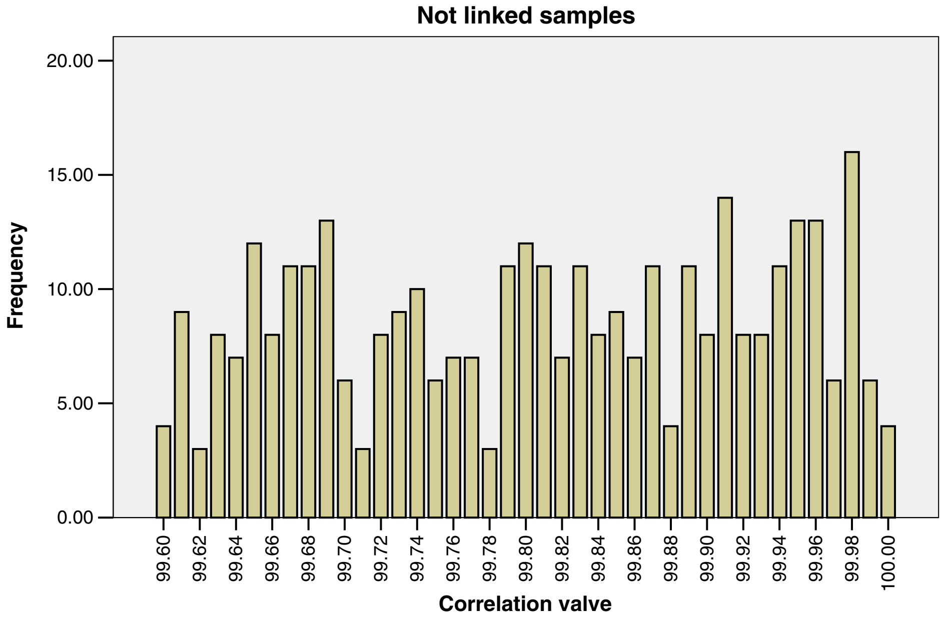

Figure 4. Distribution of correlation values between 99.60 and 100 of non-linked samples.

It was possible that in the clandestine factory, production didn't have enough chemical materials, such as acetic anhydride. So we selected six impurities (codeine, acetylcodeine, morphine, 6-monoacetylmorphine, papaverine, and noscapine) to test and analyze.

Discriminatory power of the analytical method

We chose 54 heroin samples (the total number of pairs reached 1431) from the same batch and 119 samples (the total number of pairs reached 7021) which belonged to various non-linked seizures, respectively. The correlation values of the linked samples were all higher than 99.97. Conversely, the range of correlation values of non-linked samples varied from 1 to 100 (Figure 3). The values from 99.60 to 100 showed more link probability with the risk of false positive. The distribution of interested parts (correlation values from 99.60 to 100) is shown in Figure 4.

The value of false positive was determined in this study. If we set a higher threshold of 99.97, the false positive is minimized to 0.46%. The correlation values of part non-linked samples and linked samples are plotted together in Figure 5.

Application of the method

In one scenario, the police force seized two suspects at the same time. Each one had possession of a small bag of heroin (No. 5). The correlation value of the two bags was 100. In another case (No. 6) one suspect had possession of three small bags of heroin. The correlation values of these three samples were 99.98, 99.98, and 99.99, respectively. The correlation values were all higher

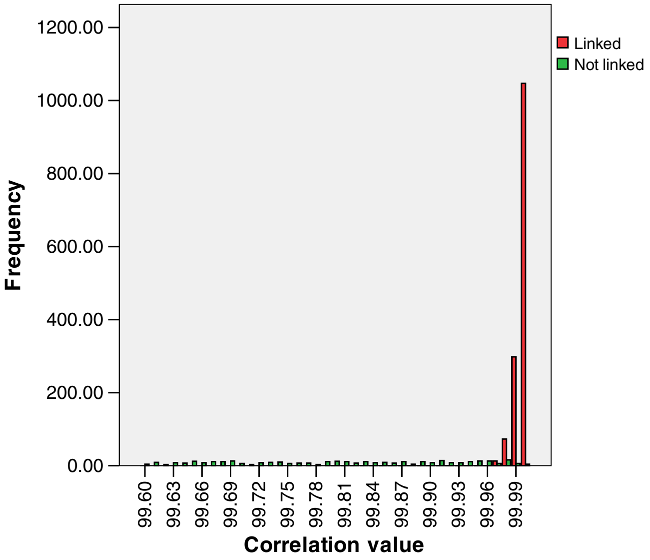

Figure 5. Overlapping plot of correlation values within linked and part non-linked samples.

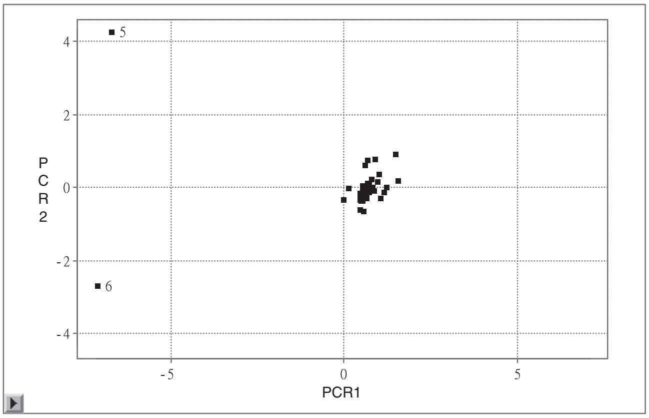

Figure 6. PC score scatter plot of the samples of No. 5 and No. 6, and 54 linked samples.

than the established threshold (99.97) and it was concluded that in each individual case (5 and 6) the respective samples originated from identical sources, which was consistent with police investigations.

The above-mentioned samples and 54 linked samples were carried out by principal component analysis (PCA) using Statistical Analysis System 9.1. Figure 6 illustrates a scatter plot of PCR2 versus PCR1 after PCA. It is obvious that there are three distinct chemical classes. Computation of the PCs resulted in the first and the second principal components describing 77.66% and 18.26% of the variance, respectively. The total variance of the two principal components accounted for 95.92% with an average of 4.08% loss of detail (Figure 7).

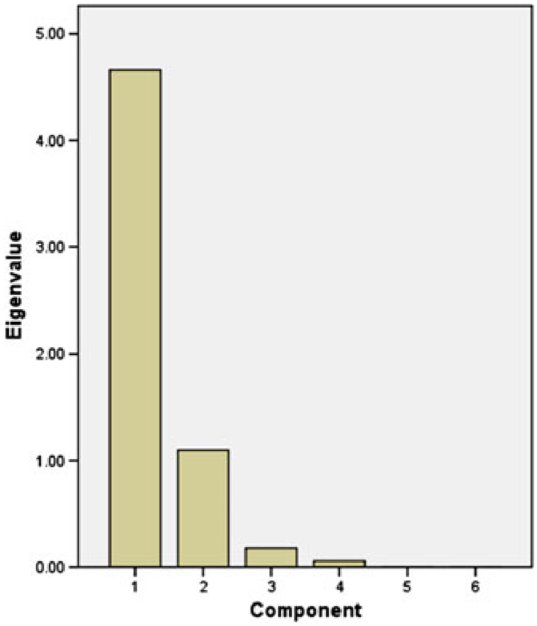

Figure 7. Scree plot of the eigen value of principal components.

Conclusions

In conclusion, this method proves to be efficient and reliable showing good discriminatory capabilities with a low false positive rate. The square cosine function represents a valuable tool to carry out illicit heroin samples comparison, which might motivate the police to reinforce the suspect links obtained during investigations. Also, the analysis result would help confirm the activity extent of trafficking and criminal networks.

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