Technical Note: Variation in chemical profiles within large seizures of cocaine bricks

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Abstract:
Cocaine is usually trafficked from South America throughout the world in packages of approximately one kilogram shaped as bricks and imprinted with a logo. Seizures consisting of multiple cocaine bricks gives the opportunity to examine the variation in the chemical profile within cocaine bricks assumed to originate from the same manufacturer and maybe even the same production batch. This knowledge may be important to the forensic investigator when chemical profiles from cocaine samples of unknown origin are compared.
In the present study, the alkaloid and residual solvent profiles from three large cocaine seizures each containing identical cocaine bricks was examined. The three cases consisted of 36, 84 and 100 cocaine bricks, respectively. Each cocaine brick was profiled according to its cocaine alkaloid and residual solvent content using gas chromatography-mass spectrometry (GC-MS) and headspace GC-MS.
The study showed that each of the three identical looking seizures consisted of up to four groups of cocaine bricks displaying the same cocaine alkaloid and residual solvent profile. The size of the groups varied from 2.4 to 63.3 kg cocaine. The study also showed that the residual solvent profile within each of the three large seizures exhibited very little variation whereas the alkaloid profile varied considerably more. This finding suggest that the same organic solvent is used for the production of several batches of cocaine HCl. Therefore, the residual solvent profile may be a tool to link different production batches from the same manufacturer even though the alkaloid profile are different.

Keywords: Illicit drugs, Cocaine, Profiling, Comparative analysis, Gas chromatography-mass spectrometry, Headspace analysis

Highlights:

The variation in chemical profiles within large seizures containing multiple cocaine bricks with the same logo was examined

198 cocaine bricks were profiled according to their alkaloid and residual solvent content

Up to four different chemical profiles were observed within the same large seizure

The residual solvent profiles are similar within large seizures assumed to originate from the same manufacturer

1. Introduction

In 2013 and 2015, Danish police seized an extraordinary large amount of cocaine. A total of 681 kg and 548 kg cocaine was seized in 2013 and 2015, respectively. These amounts opposes the more moderate seizures made in the previous years where the amount of cocaine confiscated by the police ranged between 42 and 92 kg (2006-2012 and 2014) [1]. The explanation for these peak amounts of cocaine seized in 2013 and 2015 was that, in a few cases, the seizure consisted of numerous one-kilogram cocaine bricks. In three specific cases, a large number of cocaine bricks were found by chance in containers shipped from South America. All cocaine bricks from each case were wrapped identically in multiple layers of plastic and imprinted with the same logo. Thus, these cases were assumed to originate from the same clandestine manufacturer and therefore considered suitable for examining the batch variation of clandestine cocaine production.

Limited information is available regarding the batch variation within large cocaine seizures consisting of multiple one-kilogram cocaine bricks. Earlier work has tried to link cocaine bricks imprinted with the same logo by analysing the isotopic ratios of a big seizure in Germany [2]. No correlation between the isotopic ratio and the respective logo was, however, observed. A more frequently used analytical technique in cocaine profiling is gas chromatography-mass spectrometry (GC-MS) analysis of the major and minor cocaine alkaloids [3-6] and the residual solvents [7-9] occluded in the cocaine crystals. It has been reported that the alkaloid profile of a cocaine brick can change if the brick is exposed to a heat source due to decomposition and this decomposition is proportional with the distance from the heating source [3]. The unstable nature of the alkaloid profile has also previously been reported by the authors [10].

In the present study, we examine the variation of the alkaloid and residual solvent profiles of three large seizures containing multiple cocaine bricks branded with the same logo and assumed to originate from the same clandestine manufacturer. The objective of the study is to identify different groups of chemical profiles, reflecting the presence of smaller production batches within each of the larger seizures. Furthermore, the size and variation in the chemical profile within and between these batches are examined. We discuss the possibilities of linking samples using the alkaloid and residual solvent profile within larger cocaine seizures.

2. Case material

A total of 220 cocaine bricks from three different seizures were included in the study. Each of the three seizures were confiscated from containers shipped directly from South America. It was assumed that each of the large seizures originated from the same illicit manufacturer based on the following characteristics. All cocaine bricks within each of the three seizures were wrapped in a similar manner with multiple layers of plastic and/or duct tape of similar appearance and bagged in the same type of bags. The bricks within each seizure were imprinted with the same logo (Figure 1). In addition, the cocaine bricks exhibited similar dimensions, weight, purity and presence of adulterants (Table 1). For investigation purposes, 22 of the 220 cocaine bricks were returned to the police in their original wrapping and these were therefore not included in the study. Hence, 198 cocaine bricks were subjected to profiling analysis.

Table 1 Description of the cocaine bricks in the three cases.

Case	No. of bricks	Imprinted logo	Colour	Brick size (cm)	Weight (gram)	Total weight (kg)	Purity (% w/w cocaine base)	Adulterants
A	36	"1"	White to beige	22x12x3.0-3.4	959-997	35.4	63-69	Levamisol
B	84*	"Y3"	White	23x14x3.5-4.2	1188-1213	101	69-72	-
C	100**	"f"	White	20x13x4.0	984-1033	101	72-74	Levamisol

* 12 bricks were returned to the police in their original packaging without any further analysis.

** 10 bricks were returned to the police in their original packaging without any further analysis.

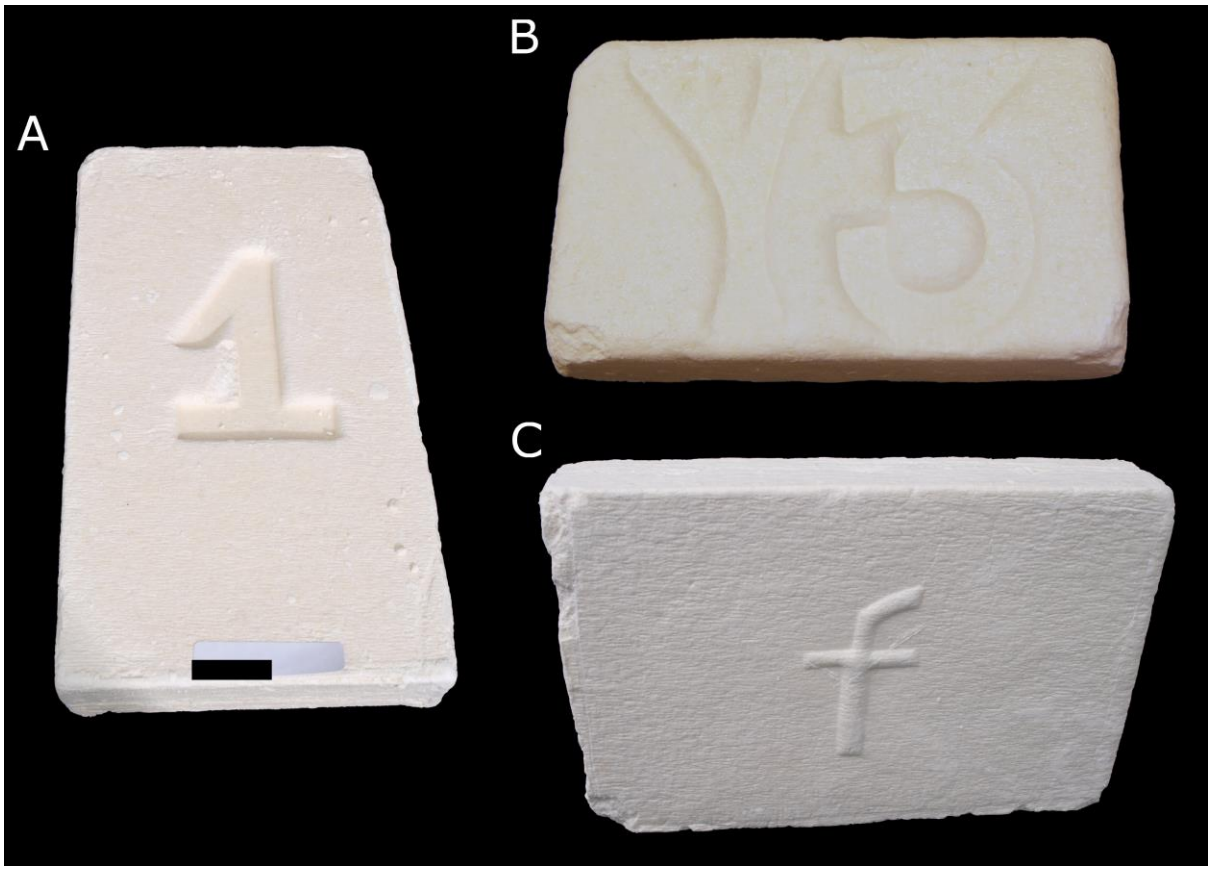

Figure 1 Imprinted logos on the cocaine bricks in case A (left), B (right, top) and C (right, bottom).

3. Materials and methods

3.1. Cocaine brick sampling

Sampling of the 198 cocaine bricks was carried out in the centre of the brick in order to avoid any potential decomposition of the chemical profile on the exterior of the cocaine bricks [3]. Thus, any exterior influences such as temperature fluctuations should have been avoided, thereby ensuring the most reliable sampling for analysis of the alkaloid profiles. A sub-sample of approximately 2-5 gram was sampled from each brick and homogenised in a mortar. Subsequently, a smaller amount of the homogenised material was used for the analysis. In addition, one randomly chosen brick was subjected to ten times randomised sampling (both interior and exterior) in order to confirm homogeneity across a brick.

3.2. Analytical methods

Two previously described GC-MS based analytical methods were used for alkaloid and residual solvent profiling [10]. Both methods are validated and accredited by the Danish Accreditation Fund (DANAK) according to the ISO 17025 standard.

3.3. Data analysis and statistics

A total of 8 alkaloid target components (Table 2) and 19 residual solvent target components (Table 3) were selected for profiling. The selected peak areas were integrated and calculated using MSD ChemStation© version E.02.00.493 and the peak area data was subsequently exported to Microsoft Excel 2013 version 15.0.4893.1000 and converted into CSV file format. All statistical analyses were performed using R version 3.3.2 and RStudio version 1.0.136. Alkaloid and residual solvent peak area data was pre-treated using log10 transformation.

The variation in chemical profiles within the three large cases was compared to the variation in 124 random seizures of cocaine made by the Danish police in the period from 2012 to 2015. A graphical representation of the sample variation is presented using principal component analysis (PCA). For each case, the pairwise cosine distances (log10 transformed) (case A: n = 630, case B: n = 2556, case C: n = 4005) between the cocaine bricks were calculated (range 0 to 1) for the alkaloid and residual solvent profile. Furthermore, the pairwise distance from each of the three large seizures to each of 124 random cocaine seizures were calculated in order to illustrate the distance between random samples. Finally, the pairwise cosine distances (n = 45) within a single cocaine brick were also calculated.

Table 2 Target compounds used for the profiling of cocaine alkaloids and their relative retention time (RRT).

#	Compound	RRT
IS	Nonadecane (internal standard)	1.00 (RT 17.3 min)
1	Ecgonine methylester (EME)	0.71
2	Ecgonine (EC)	0.79
3	Tropacocaine (TROPA)	1.04
4	Benzoylecgonine (BENZO)	1.23
5	Norcocaine (NOR)	1.24
6	Cis-cinnamoylcocaine (CIS)	1.29
7	Trans-cinnamoylcocaine (TRANS)	1.38
8	3,4,5-Trimethoxycocaine (TMC)	1.63

Table 3 Target compounds used for the profiling of the residual solvents and their retention time (RT).

#	Compound	RT (min)
1	Diethyl ether	3.16
2	Acetone	3.51
3	Isopropyl alcohol	3.89
4	n-Pentane	4.04
5	Dichloromethane	4.15
6	n-Hexane	5.03
7	2-Butanone	6.61
8	Ethyl acetate	6.75
9	Cyclohexane	7.99
10	Benzene	8.98
11	n-Heptane	10.32
12	Methyl cyclohexane	12.15
13	n-Propyl acetate	13.16
14	Toluene	15.50
15	Isobutyl acetate	16.22
16	Mesityl oxide	17.76
17	m-Xylene	19.55
18	o-Xylene	20.81
19	Mesitylene	23.25

4. Results and discussion

The PCA score plots in Figure 2 show the distribution of the chemical profiles for the three large seizures of cocaine bricks together with 124 random cocaine seizures analysed routinely in our laboratory from 2012 to 2015. The figure provides a visual representation of the distribution of the chemical profiles from the three large seizures relative to the general profile distribution for random seizures. The distribution of samples observed in the PCA plot indicates that two out of the three large seizures consist of various minor groups with the same alkaloid profile. The PCA plot indicates one alkaloid profile for case A, four different profiles for case B (designated B1 – B4) and two alkaloid profiles for case C (designated C1 and C2) (Figure 2 top). Hence, two of the large seizures, case B and C, may possibly contain several smaller groups of varying size, which can be separated based on their alkaloid profile. Unlike the distribution of the alkaloid profiles in the PCA score plot, only a single profile is observed for the residual solvents for each of the three seizures (Figure 2 bottom).

Some of the profiles from the random samples (grey points) seem to group close together with some of the profiles from the three large seizures in Figure 2. This might suggest that some of the random samples are linked to the large seizures. However, when comparing both the alkaloid and residual solvent profiles from the 124 random samples with the large seizures, none of the samples is in fact linked to any of the large seizures. About 70% of the variation between the chemical profiles is explained by PC1, PC2 and PC3, and the samples may therefore be further separated when performing comparative analysis based on the remaining 30%, which cannot be illustrated in the three-dimensional PCA plot. The possibility that samples of different origin have common alkaloid or residual solvent profiles by chance can however not be ruled out.

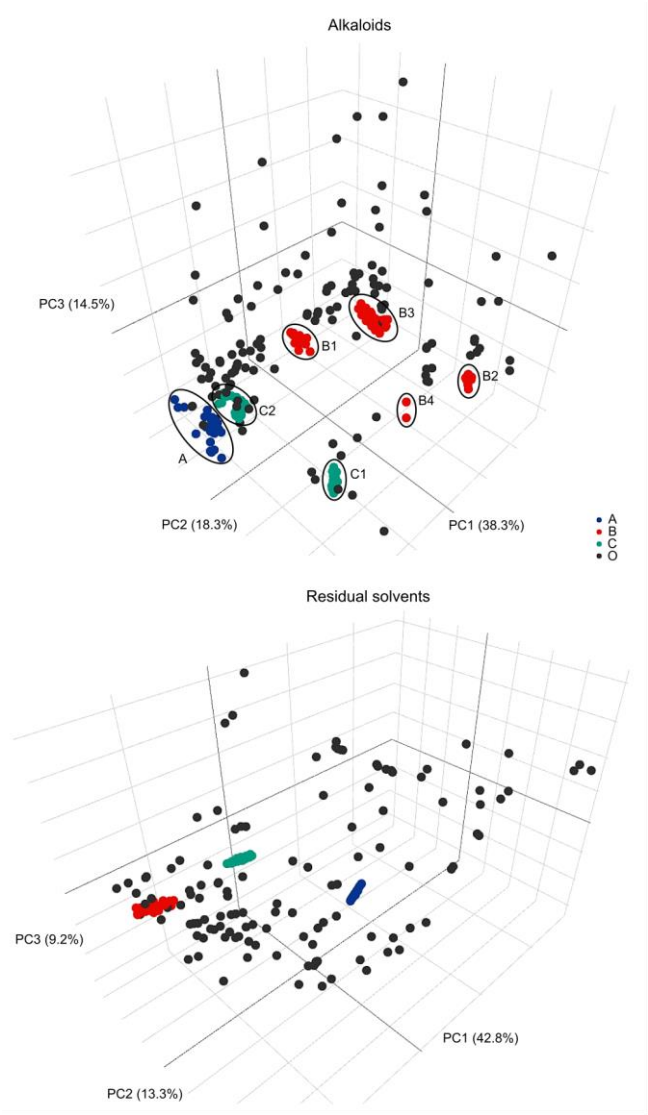

Figure 2 PCA score plots for the three large seizures (A, B and C) together with 124 random cocaine seizures (O) analysed between 2012 and 2015. Top: Alkaloid PCA score plot. The individual groups observed within case B and C are depicted. Bottom: Residual solvent PCA score plot.

To support the observations obtained from the PCA plots, the pairwise cosine distances (range 0 – 1) between the samples within each of the large seizures (Table 4) was calculated. Also, the mean distances from each of the identified groups to the 124 random cocaine seizures is presented in the table. This has been done to give an impression of the relative distances between linked samples and random samples. For each of the large seizures, only minor variation between the residual solvent profiles is observed, whereas larger variation is found between the alkaloid profiles. It also appears that the mean pairwise alkaloid profile distances within each sub-group identified from the PCA score plot (B1 – B4, C1 and C2) are considerably lower than within the entire case. Multiple samplings from a single cocaine brick (n=10) was performed to test for inhomogeneity across a brick. In this case, a mean alkaloid and residual solvent cosine distance of 0.006 was observed, corresponding to the distances observed between the bricks in an entire group (results not shown). The distribution of the pairwise distances between the profiles is presented in Figure 3. For case B, the largest distance between two samples from the same seizure is observed (pairwise distance of 0.17). The

corresponding chromatograms for the alkaloid and residual solvent profiles for these two samples are shown in order to give an impression of how the corresponding chemical profiles look (Figure 4 and 5).

Table 4 Mean, minimum and maximum pairwise cosine distances (range 0 - 1) between the alkaloid and residual solvent profiles within each of the large seizures (within the group) and between the large seizures and 124 random cocaine seizures (to random seizures). The groups presented underneath case B and C (B1 – B4 and C1 – C2) is based upon the alkaloid PCA score plot in Figure 2.

	mean distance (min – max) within the group		mean distance (min – max) to random seizures		no. of bricks	amount (kg)
Alkaloids						
Case A	0.002	(0.0 – 0.1)	0.1	(0.004 – 0.5)	36	35.4
Case B	0.05	(0.0 – 0.2)	-		72	86.2
Group B1	<0.001	(<0.001 – 0.003)	0.1	(0.001 – 0.4)	12	14.4
Group B2	<0.001	(<0.001 – 0.004)	0.2	(0.002 – 0.6)	15	18
Group B3	0.002	(<0.001 – 0.008)	0.2	(0.002 – 0.5)	43	51.4
Group B4	0.001	-	0.2	(0.001 – 0.5)	2	2.4
Case C	0.02	(0.0 – 0.06)	-		90	90.5
Group C1	<0.001	(0.0 – 0.003)	0.2	(0.001 – 0.6)	63	63.3
Group C2	<0.001	(<0.001 – 0.003)	0.1	(0.001 – 0.4)	27	27.2
Residual solvents						
Case A	<0.001	(<0.001 – 0.002)	0.4	(0.1 – 1)	36	35.4
Case B	<0.001	(<0.001 – 0.002)	0.2	(0.002 – 1)	72	86.2
Case C	<0.001	(<0.001 – 0.001)	0.2	(0.05 – 1)	90	90.5

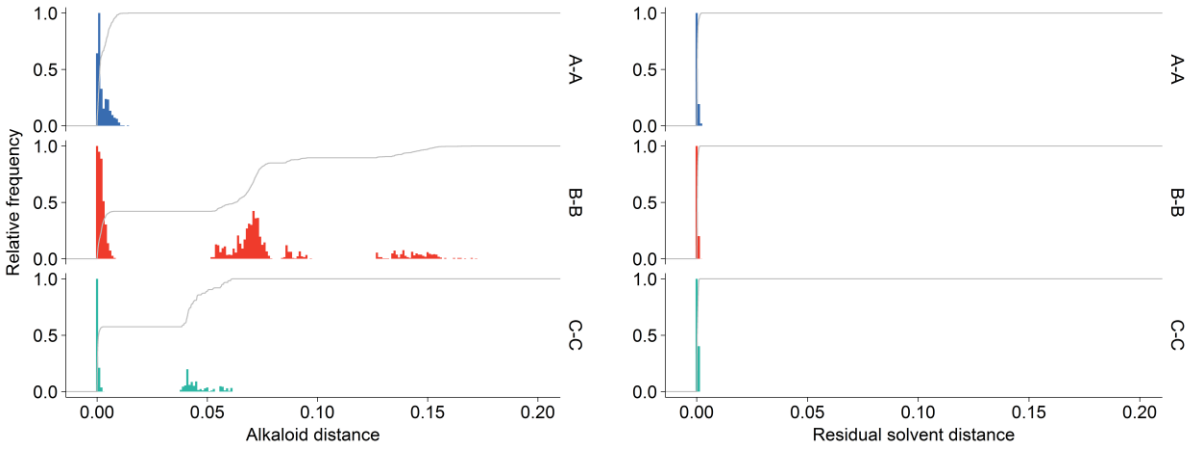

Figure 3 Distribution of all pairwise cosine distances within each of the three large seizures A, B and C. Alkaloid distances (left) and residual solvent distances (right).

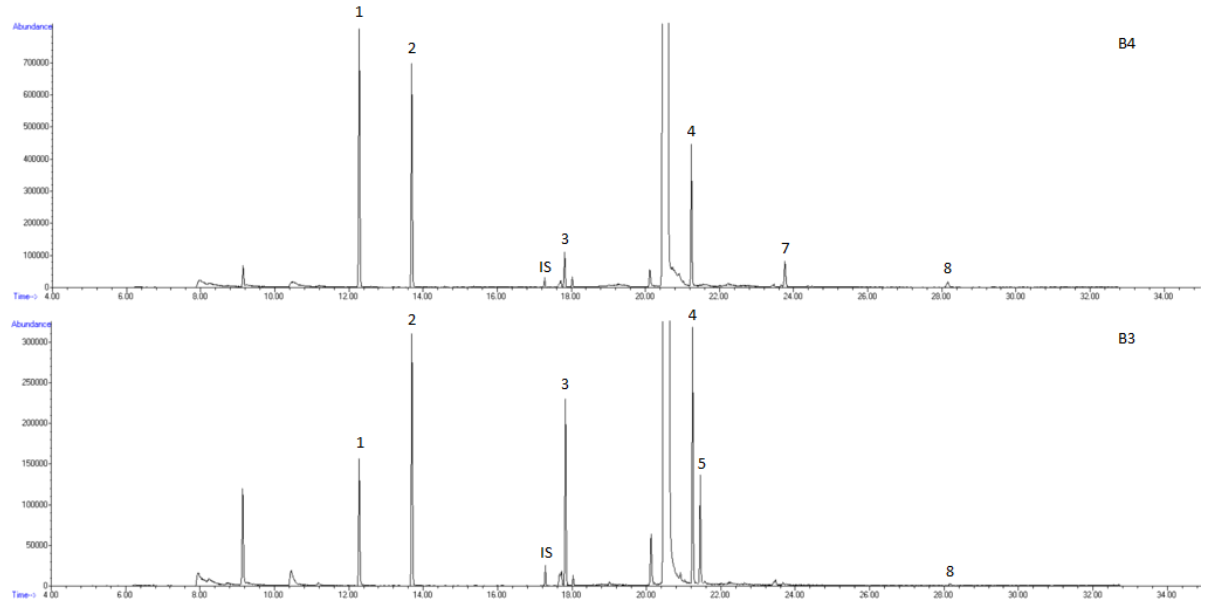

Figure 4 Chromatograms showing the alkaloid chemical profiles of the two alkaloid samples with the highest cosine distance between them. The two samples originate from case B. Top: Alkaloid profile for sample 1 (group B4). Bottom: Alkaloid profile for sample 2 (group B3). The peaks are as follows: (1) ecgonine methylester, (2) ecgonine, (3) tropacocaine, (4) benzoylecgonine, (5) norcocaine, (6) cis-cinnamoylcocaine, (7) trans-cinnamoylcocaine, (8) 3,4,5-trimethoxycocaine.

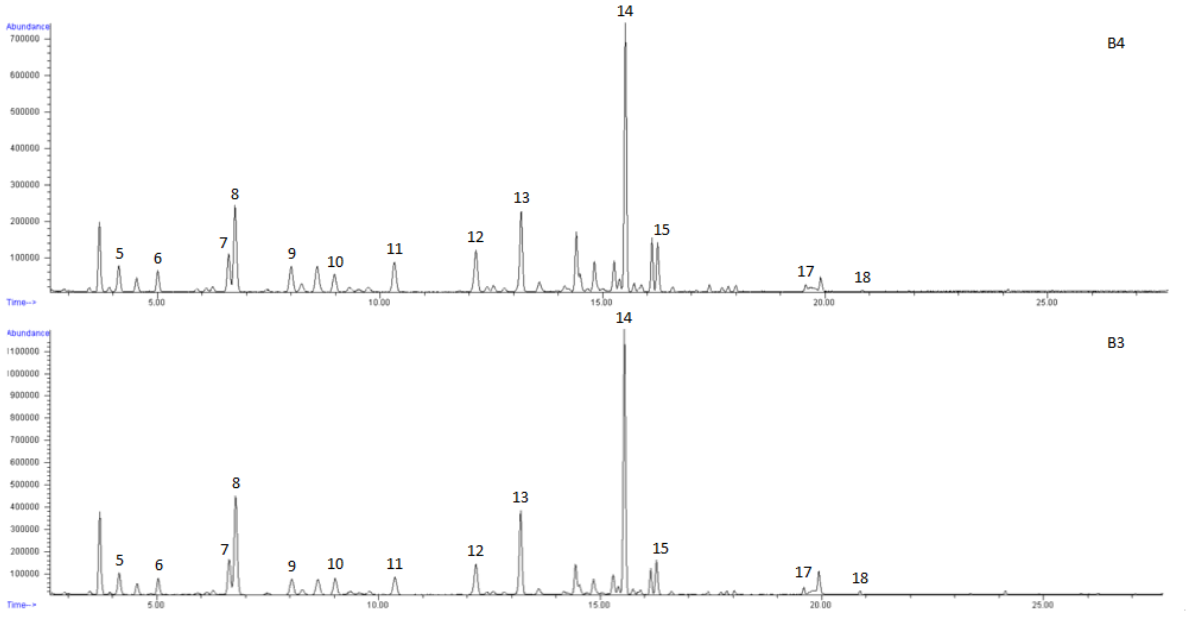

Figure 5 Chromatograms showing the residual solvent chemical profiles of the two samples with the highest cosine distance between them. The two samples originate from case B. Top: Residual solvent profile for sample 1 (group B4). Bottom: Residual solvent profile for sample 2 (group B3). The peaks are as follows: (1) diethyl ether, (2) acetone, (3) isopropyl alcohol, (4) n-pentane, (5) dichloromethane, (6) n-hexane, (7) 2-butanone, (8) ethyl acetate, (9) cyclohexane, (10) benzene, (11) n-heptane, (12) methyl cyclohexane, (13) n-propyl acetate, (14) toluene, (15) isobutyl acetate, (16) mesityl oxide, (17) m-xylene, (18) o-xylene, (19) mesitylene.

The results presented in this study indicate that large seizures of cocaine may contain a number of smaller groups (or batches) based on the appearance of the alkaloid chemical profiles. In contrast, the chemical profile of the residual solvents only show little variation throughout the seizure. These findings may very well reflect the production process by which illicit cocaine is commonly manufactured [11]. Accordingly, several batches of coca paste or coca base may be purified into cocaine HCl using/reusing the same organic solvent mixture, resulting in multiple cocaine bricks with identical solvent profiles. Bricks with common alkaloid profile may comprise up to 63 kg of cocaine (group C1) although smaller groups of approximately 2 kg cocaine was identified. The different groups of alkaloid profiles found within the large seizures may possibly result from the processing of different batches of coca paste or coca base with the same organic solvent mixture. However, inhomogeneity within a large production batch could also lead to differences in the alkaloid profiles.

From a forensic perspective, the present study illustrates that residual solvent profiles may be a tool to link cocaine bricks or seizures to a common production source even though the alkaloid profiles differ. Several alkaloid profiles may be present in large seizures of cocaine, which at first appears to be similar by its physical appearance. In such cases, the residual solvent profiles may still be a tool to link the samples together. This knowledge may contribute to an alternative interpretation of chemical profiles where samples may originate from different production batches made by the same manufacturer. Caution should however be taken as different manufactures could possibly share the same organic solvent mixture. Hence, such linkage should be combined with other types of case related evidence.

Within the large seizures, smaller groups or batches varied from 2 kg up to 63 kg. Large batches displaying the same alkaloid and solvent profile such as the group containing 63 kg cocaine can give rise to thousands of cocaine sale packages at the consumer level. In this perspective, chemical profiling can be a strong forensic tool to unravel distribution networks for investigative purposes.

5. Conclusion

The present study describes the variation of the alkaloid and residual solvent profiles within three large seizures containing multiple one-kilogram cocaine bricks assumed to originate from the same clandestine manufacturer. The residual solvent profiles exhibited considerable lower variation compared to the alkaloid profiles. One group was observed for the residual solvent profile within the individual cases, while one to four groups were observed for the alkaloid profile. Hence, our findings indicate that the same organic solvents are being used/reused for extracting multiple batches of cocaine HCl in the clandestine laboratory and this production approach is reflected in the chemical profiles. Several alkaloid profiles may be present in large cocaine seizures, which at first seem to have a common origin. In such cases, the residual solvent profiles can still be used in combination with other types of evidence to link the samples together.

6. References

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