5.6 Profiling of Trace Elements by ICP-MS

After determining the major components and manufacturing impurities in the heroin samples, the remaining portions were subjected to the quantification of trace elements using inductively coupled plasma-mass spectrometry (ICP-MS). The subtasks include: 1) ICP-MS method validation, 2) statistical validation of ICP-MS data using 6 batches of related samples, and 3) analysis of case samples for the identification of the possible source of metal contamination as well as for the purpose of sample classification (street level sample-to-sample comparison).

5.6.1 ICP-MS Method Validation

ICP-MS is a well established technique which usually does not require extensive optimization. However, method validation is crucial to ensure that the method is suitable for the analytical purpose.

Trace elements present in illicit heroin are assumed to have been primarily introduced as contaminants from three sources, namely the processing method, cooking utensils and water used in the cutting process. For example, sodium (Na) and calcium (Ca) are usually the cations of the substances (sodium bicarbonate and lime) added during processing (Zerel *et al.*, 2005). On the other hand, iron (Fe) can be introduced from the rusty piping system or cooking utensils. When water is added together with the adulterants during the cutting process, the illicit heroin can acquire contaminants in the form of trace elements from the drinking water. In this task, a total of 20 trace elements were tentatively chosen for the validation study. In the following discussion, Na, magnesium (Mg), potassium (K), Ca and Fe are grouped as major elements as they are usually present in high levels. The remaining elements (except mercury, Hg) are considered as minor elements. Hg is seldom present in tap water and its level (if present) is normally lower than that of the minor elements.

5.6.1.1 Repeatability and Reproducibility

As with the chromatographic technique, intra-day precision (repeatability) and inter-day precision (reproducibility) must be validated to ensure that the ICP-MS is in a good working condition. The performance of the instrument was confirmed with a mixture of standard elements and the QC sample. The concentration of each element was measured relative to the IS chosen according to the group of elements (Table 5.52). On this basis, the RSD was also computed to evaluate the precision of each element.

Table 5.52: RSD (%) for the repeatability and reproducibility of 20 elements in a mixed standard and a QC sample

Group	**Element**	**Ion, m/z**	**Repeatability (n = 8)**		**Reproducibility (n = 8)**	
			Standard[a]	**QC sample[b]**	**Standard[a]**	**QC sample[b]**
I	B	11	0.11	3.16	0.26	3.59
	(Na)	23	0.03	2.50	0.09	2.34
	(Mg)	24	0.02	2.43	0.12	3.90
	Al	27	0.16	3.04	0.26	2.78
	(K)	39	0.02	3.05	0.12	3.57
	(Ca)	44	0.02	2.71	0.06	4.59
	Sc	45	**IS-I[c]**			
II	Cr	52	0.08	2.33	0.23	2.51
	Mn	55	0.08	3.16	0.20	3.30
	(Fe)	57	0.03	4.01	0.05	2.05
	Ni	60	0.12	4.46	0.14	1.80
	Cu	63	0.10	3.67	0.19	2.16
	Zn	64	0.09	4.14	0.24	2.34
	As	75	0.09	4.20	0.39	2.99
	Se	82	0.12	5.03	0.19	5.17
	Rh	103	**IS-II[c]**			
III	Ag	107	0.07	3.10	0.08	4.55
	Cd	114	0.10	2.82	0.13	3.66
	In	115	**IS-III[c]**			
IV	Sb	123	0.08	3.19	0.14	4.24
	Ba	138	0.07	1.72	0.18	5.27
	Hg	202	0.59	8.64	2.43	14.05
	Pb	208	0.09	2.74	0.13	5.81
	Bi	209	**IS-IV[c]**			

[a] Major elements in parentheses at 10 ppm, minor elements at 0.1 ppm and Hg at 0.005 ppm.
[b] Major elements in parentheses at 5 ppm, minor elements at 0.05 ppm and Hg at 0.0025 ppm.
[c] IS was maintained at 0.01 ppm. Individual signal relative to the IS is used for concentration calculation. Each IS is responsible for different groups indicated by its suffix I to IV.

According to Table 5.52, all the elements in both the standard and QC samples are repeatable with an RSD < 6% (except for Hg, RSD < 9%) and reproducible with an RSD < 6% (except for Hg, RSD < 15%) whereby the RSD < 20% is considered as acceptable in this study. The acceptable limit is set at this level in order to accommodate the trace levels of analytes which are usually present in the ppb to ppm levels. The QC sample showed relatively high values of RSD as the elements were prepared at lower concentration levels. Since Hg was analyzed at an even lower level, the relatively poor inter-day precision (RSD < 15 %) is still considered as acceptable. Generally, the instrument was found to be stable for elemental analysis as there are no apparent systematic errors in the precision studies.

5.6.1.2 Linearity, LOD and LOQ

A linear response of the detector over a selected concentration range is preferred in quantitative analysis. Since some elements were not detected at the trace levels, the lower limit for the linear range was fixed at the concentration that shows the presence of the target element in at least two injections. A regression line was constructed for each linear range and all the elements achieved an $r^2 \geq 0.9975$ (except for Hg, $r^2 = 0.9938$), which is sufficiently linear for quantitative analysis (Table 5.53).

The LOD and LOQ may sometimes vary according to the specific purpose (Thompson, Ellison & Wood, 2002; UNODC, 2009c). In this study, the LOD and LOQ are redefined to fit the profiling purpose. The LOD was defined as the level that gives not more than 50% false negative results whereas the LOQ should fall within the acceptable precision exhibited by the instrument (which is RSD < 15%, the maximum RSD for the reproducibility determined in Section 5.6.1.1 Repeatability and Reproducibility).

From the series, the LOD was determined based on the lowest concentration level at which the element was detected ≥ 3 times out of the six injections so that it can fit within the linear range (the lower limit of the linear range begins at the concentration level that shows the presence of the analyte from at least 2 injections). Depending on the elements in Table 5.53, the LODs ranging from 0.0001 – 1 ppb were obtained for all the elements except for Ca (LOD = 100 ppb). These LODs are sufficiently adequate for the detection of the target trace elements. Ca is usually present in high levels and thus the obtained LOD is acceptable for this study.

The LOQ was grossly estimated from the dilution series prepared. The initial LOQ was determined as that when the element showed an RSD < 15% from the six injections. For the minor elements and Hg in Table 5.53, the LOQs ranging from 0.1 – 1 ppb were obtained. In the case of the major elements, the LOQs from 1 – 10 ppb were observed except for K and Ca which showed LOQs at 100 ppb and 500 ppb respectively. In profiling studies, the LOD is more important than the LOQ since the absolute concentration value of the element is not critical.

As most data points were clustered at the bottom of the plot, it was decided to re-evaluate the r^2 values using bilogarithmic plots. The new plot indicated that boron (B), K and Hg had a relatively poorer r^2 value. The value can be improved when the LOD and the lower limit were reset at 0.1 ppb, 1 ppb and 0.001 ppb respectively for the three elements. Hence, all the elements were able to achieve an $r^2 > 0.9$, and this indicates that the chosen concentration ranges (and the new range for B, K and Hg) are sufficiently good for elemental analysis.

Table 5.53: Analytical figures of merit (n = 6)

Element	**LOD[a] (ppb)**	**LOQ[b] (ppb)**	**Concentration range covered[c] (ppb)**	**Linearity function**	**Correlation coefficient, r^2**	
					Original[d]	**Log[e]**
B	0.001	1	0.001 – 1000	y = 1.0765x + 10.416	0.9996	0.8032[f]
(Na)	1	10	0.1 – 10000	y = 1.0092x + 20.542	0.9999	0.9937
(Mg)	1	1	0.1 – 10000	y = 0.9867x + 18.053	1.0000	0.9868
Al	0.001	1	0.001 – 1000	y = 0.8058x + 5.9559	0.9988	0.9007
(K)	0.01	100	0.01 – 10000	y = 0.9625x + 0.6279	1.0000	0.7566[f]
(Ca)	100	500	100 – 10000	y = 0.9407x + 20.894	0.9997	0.9798
Cr	0.001	0.1	0.001 – 1000	y = 0.8825x + 3.5462	0.9997	0.9231
Mn	0.001	0.1	0.001 – 1000	y = 0.9236x + 2.7364	0.9998	0.9761
(Fe)	0.01	10	0.01 – 10000	y = 0.9781x + 48.953	0.9983	0.9253
Ni	0.001	0.1	0.001 – 1000	y = 0.9126x + 5.1069	0.9975	0.9827
Cu	0.1	1	0.1 – 1000	y = 0.8999x + 4.0018	0.9998	0.9916
Zn	0.001	1	0.001 – 1000	y = 0.9229x + 4.4287	0.9985	0.9285
As	0.1	1	0.01 – 1000	y = 0.9924x + 1.6531	0.9999	0.9991
Se	0.01	1	0.001 – 1000	y = 0.9997x + 1.073	1.0000	0.9778
Ag	0.001	1	0.001 – 1000	y = 0.9830x - 1.6905	0.9999	0.9653
Cd	0.01	0.1	0.001 – 1000	y = 0.9157x + 3.3456	0.9992	0.9987
Sb	1	1	1 – 1000	y = 0.9555x + 3.7481	0.9996	0.9996
Ba	0.001	0.1	0.001 – 1000	y = 0.9537x + 1.5333	0.9999	0.9782
Hg	0.0001	0.1	0.0001 - 100	y = 0.6588x - 0.5755	0.9938	0.8995[f]
Pb	0.001	0.1	0.001 – 1000	y = 0.9793x + 0.8338	1.0000	0.9914

[a] LOD was decided based on the lowest concentration that allowed the element to be detected in at least three injections out of six.

[b] LOQ was decided based on the lowest concentration that showed an RSD < 15 % (the maximum repeatability and reproducibility obtained) from the six injections.

[c] The lower limit of the range was decided when at least two injections showed the presence of the element.

[d] r^2 values derived from conventional plots (response against concentration).

[e] r^2 values derived from bilogarithmic plots (log response against log concentration).

[f] The r^2 value can be improved to > 0.9 when the LOD and lower limit of the concentration range are increased to 0.1 ppb (B), 1 ppb (K) and 0.001 ppb (Hg).

5.6.1.3 Accuracy as Measured by Recovery

The accuracy of the method was assessed by recovery tests. The mean recoveries for the target elements are displayed in Table 5.54. All the elements showed a mean recovery between 92% and 108% except for silver, Ag (68%) and Hg (78%). Due to the poor recoveries of the latter two elements, they were then excluded for further analysis as the method is not suitable for these elements. Their low recoveries could be due to two reasons: 1) absorption by the plastic vessels used in the analysis and 2) interference from the sample matrix. Hence, the remaining 18 elements were used for subsequent investigation.

Table 5.54: Recovery (%) for 20 trace elements from the street heroin sample matrix

Element	**High**	**Medium**	**Low**	**Mean**	**Standard deviation**
B	103.05	98.05	97.74	99.61	2.98
(Na)	103.27	90.62	85.44	93.11	9.17
(Mg)	101.37	94.80	88.24	94.80	6.56
Al	101.74	95.82	100.40	99.32	3.10
(K)	98.66	91.47	87.11	92.41	5.83
(Ca)	101.78	94.65	84.19	93.54	8.85
Cr	93.56	95.21	92.50	93.76	1.37
Mn	91.75	95.73	90.75	92.74	2.64
(Fe)	97.49	101.44	94.77	97.90	3.35
Ni	98.45	101.92	97.04	99.14	2.51
Cu	102.10	105.57	99.31	102.32	3.13
Zn	104.04	104.81	104.41	104.42	0.39
As	111.36	102.97	107.21	107.18	4.20
Se	95.83	73.94	108.21	92.66	17.36
Ag	84.21	77.02	42.35	67.86	22.38
Cd	99.41	100.88	102.97	101.09	1.79
Sb	99.78	102.82	102.60	101.73	1.69
Ba	102.51	105.79	105.68	104.66	1.86
Hg	92.43	75.02	66.62	78.02	13.17
Pb	100.59	102.36	101.31	101.42	0.89

5.6.1.4 Sample Precision

It is more appropriate to assess the precision of the ICP-MS readings with the presence of sample matrix. Three random heroin case samples (marked ‘X’, ‘Y’ and

'Z') were selected to assess the sample precision based on the RSD. As indicated in Table 5.55, certain elements performed satisfactorily well with low RSD values in one sample, but sometimes badly with high RSD values in another sample. For example, barium (Ba) has a significantly poorer RSD value in Sample X compared to Samples Y and Z for the intra-sample precision. This was probably due to the matrix effects from the different samples. By excluding the outliers, the mean values of the intra-sample and inter-sample precision showed RSD values of < 5% and < 14% respectively.

Table 5.55: Sample precision in RSD (%) and r^2 determined from three random samples

Element	**Intra-sample precision (n = 6)**			**Inter-sample precision (n = 12)**		
	X	**Y**	**Z**	**X**	**Y**	**Z**
B	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
(Na)	0.75	1.24	10.62	2.00	15.28	**36.37**
(Mg)	1.97	3.99	1.91	5.87	**64.02**	2.41
Al	8.09	5.11	11.49	22.98	**51.70**	12.65
(K)	**30.23**	**33.08**	N.D.	**35.68**	**33.38**	N.D.
(Ca)	1.62	2.59	3.75	2.72	21.35	2.22
Cr	0.65	1.54	2.23	2.17	6.52	16.73
Mn	1.22	0.91	1.12	1.40	3.28	1.89
(Fe)	N.D.	N.D.	4.23	N.D.	N.D.	12.63
Ni	7.49	5.24	2.13	17.48	**58.93**	5.16
Cu	N.D.	2.26	10.75	N.D.	**74.11**	**31.94**
Zn	0.93	1.18	1.48	1.73	5.44	3.01
As	N.D.	N.D.	2.97	N.D.	N.D.	2.80
Se	N.D.	N.D.	3.04	N.D.	N.D.	2.78
Cd	13.06	14.40	6.77	11.39	27.02	7.23
Sb	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Ba	**46.76**	8.29	3.97	28.15	**49.39**	8.16
Pb	1.61	1.28	3.78	2.98	**34.19**	6.94
Mean	**9.53**	**6.24**	**4.68**	**11.21**	**34.20**	**10.19**
Mean (excluding outliers)	**3.74**	**4.00**	**4.68**	**8.99**	**13.15**	**6.51**
Pearson correlation, r^2	**1.000**	**1.000**	**0.999 – 1.000**	**1.000**	**0.998 – 1.000**	**0.996 – 1.000**

N.D. = Not detected
Note: Figures in bold indicate unacceptable RSDs as defined by Myors *et al.* (1998).

The acceptable sample RSD and r^2 defined by Myors *et al.* (1998) are RSD $\leq$ 30% and $r^2 \leq 70\%$ respectively. Many of the elements analyzed have fulfilled these conditions in at least one sample in both the intra-sample and inter-sample categories except for K and copper (Cu). With regard to K, acceptable RSD values could not be obtained in both the categories whereas for Cu it was only achieved in the intra-sample category. To assess the extent to which this variation can affect sample-to-sample comparison, the r^2 value was used to assess the correlation between the related samples based on the detected elements. All the related samples achieved an $r^2 \geq 0.996$ despite the variation. This implies that the method is capable of clustering related samples despite the measurably high RSD values.

5.6.1.5 Sample Weight Test

Hypothetically, a larger weight of sample will offer a better precision (RSD) for the findings. To test this hypothesis, a preliminary study on the sample weight was carried out using a relatively high purity sample (marked ‘H’) and low purity sample (marked ‘L’). The performance of the samples is presented in Figure 5.64. It was found that high RSD values were more frequently associated with sample H irrespective of the weight. Sample L however performed very much better except for B (marked ‘Q1’) and antimony (Sb) (marked ‘Q2’) using L40. The reason for Sample H performing worse than Sample L may be attributed to the sample homogeneity. High purity samples usually contain high amounts of natural alkaloids which are sticky and make homogenizing difficult. For highly cut samples such as Sample L, the stickiness is overcome by the presence of adulterants that are mixed during the cutting process, making the whole sample readily homogeneous. In addition, it is also inferred that higher sample weights do not necessarily offer better RSD values. In fact, the errors associated with trace elements are not easily overcome by the sample weight at the milligram level. Despite this problem, most elements showed sufficient precision with RSD < 20% (Figure 5.64). This indicates that sufficient precision can be afforded by any of the weights.

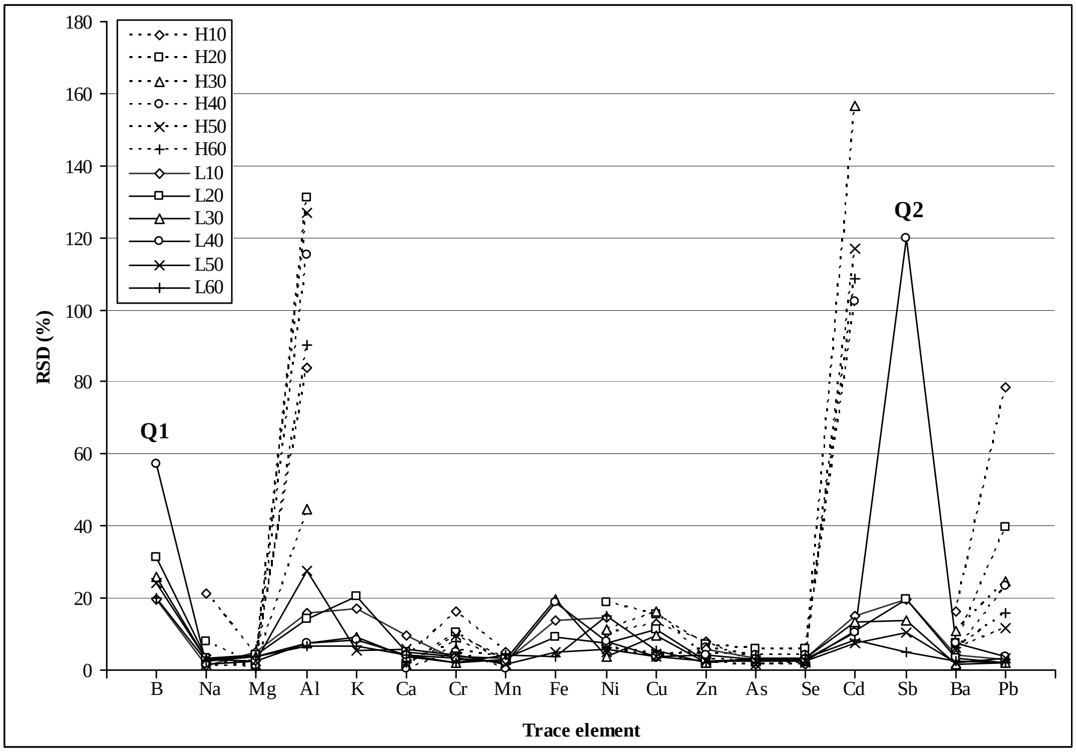


Figure 5.64: RSD of a high purity sample (dotted line) and low purity sample (black line) analyzed at six different weights (The disconnection of the line indicates the absence of the element)

As some of the elements were not detected at low sample weights (e.g. 10 mg), the use of a higher weight (e.g. 50 mg) for case sample analysis was recommended. However, this sample weight resulted in analyte saturation (especially Na) and rendered the solution too colloidal (particles in suspension). Alternatively, the use of 30 mg as an initial weight was employed in this study. Sample dilution may be required for samples showing saturated Na at 30 mg.

5.6.1.6 Dissolution Vessels

It is vital to determine the level of contamination by trace elements in a commercial tube so that extra measures can be taken to minimize the errors arising from this contamination. Two types of plastic tubes were employed in this study. Type J was a sterile tube while Type H was non-sterile with both of the 15 mL capacity. For each type, two random tubes were sampled, to which 10 mL of 1% HNO_3 solution was added without prior rinsing. From the analysis, Type H appeared to be much cleaner with only arsenic (As) and selenium (Se) (0.33 – 1.23 ppb) detected in the tube. Type J on the other hand displayed the presence of Na, aluminium (Al), Ca, chromium (Cr), manganese (Mn), Fe, Cu, As, Se, Ba and lead (Pb) in the range of 0.01 – 25.65 ppb. This study suggests the need for prior rinsing (with at least two volumes of nitric acid) before the tube is used for sample dissolution.

5.6.1.7 Sample Filtration

For high throughput analysis, direct sample dissolution is preferred as it can eliminate the tedious sample preparation procedure. However, when this method is employed, small particles may be present in the solution. Hence, the solution must be filtered before it is directly aspirated into the instrument. However, this additional step of filtration can impart errors to the readings as the filter paper may introduce contaminants and/or absorb the target analytes from the filtering solution. Therefore, three random samples labeled ‘1’, ‘2’ and ‘3’ were chosen to estimate these errors. Each sample was prepared in a 50 mL plastic bottle. The solution is poured into two plastic tubes directly. Two other tubes fitted with filter papers (which were rinsed with deionized water) were employed for filtering the solution. To estimate errors associated with the filtration, the concentration difference between the results obtained with the filtered solution and the direct dissolution was computed as follows: the mean concentration of each element from the two filtered solutions minus the mean concentration of that element from the two direct dissolutions. Based on this, the direct dissolution serves as a basis to estimate the deviation of the reading from that of the filtered solution. The resulting positive value suggests additional effects due to contamination whereas the negative value indicates absorptive losses. The concentration differences of the elements in the three samples are summarized in Table 5.56. High levels of contamination were associated with Na, magnesium (Mg), K and Ca. A significant absorptive loss of Se was occasionally observed. The other elements showed insignificant contamination and losses. From these results, filtered samples are not suitable for accurate quantification.

Table 5.56: Concentration differences of the elements from three samples

Element	**Concentration difference (ppb)**		
	1	**2**	**3**
B	N.D.	N.D.	N.D.
Na	1230.10	737.31	1235.16
Mg	46.64	31.90	50.84
Al	2.34	2.41	3.82
K	20.30	25.03	0.00
Ca	232.58	100.24	301.69
Cr	-0.46	-0.52	-0.65
Mn	0.63	0.24	0.76
Fe	2.96	7.08	9.05
Ni	0.65	0.39	0.59
Cu	3.71	2.51	3.70
Zn	-3.46	-2.45	0.56
As	0.00	-0.04	-8.73
Se	-0.09	-0.16	-32.89
Cd	0.01	0.00	0.00
Sb	N.D.	N.D.	N.D.
Ba	1.69	1.70	2.37
Pb	0.10	0.06	0.12

N.D. = Not detected

As the aim of this study is to profile and cluster the samples, it would be beneficial to evaluate whether the contamination and losses will impart significant effects on the classification outcome. To this end, HCA was performed to classify the 12 solutions using the obtained ICP-MS data (that were tentatively subjected to standardization to minimize the influence of high concentration elements). According to Figure 5.65, the dendogram illustrates that both the direct (designated ‘D’) and filtered (designated ‘F’) solutions were successfully clustered within their respective groups (indicated by the dark dotted square boxes) except for Sample 1F. This infers that to some extent the elemental profiles of the filtered solutions are still useful in sample grouping despite the errors introduced from the filtration. The reliability of the ICP-MS data will again be statistically evaluated using a larger number of samples in the subsequent section.

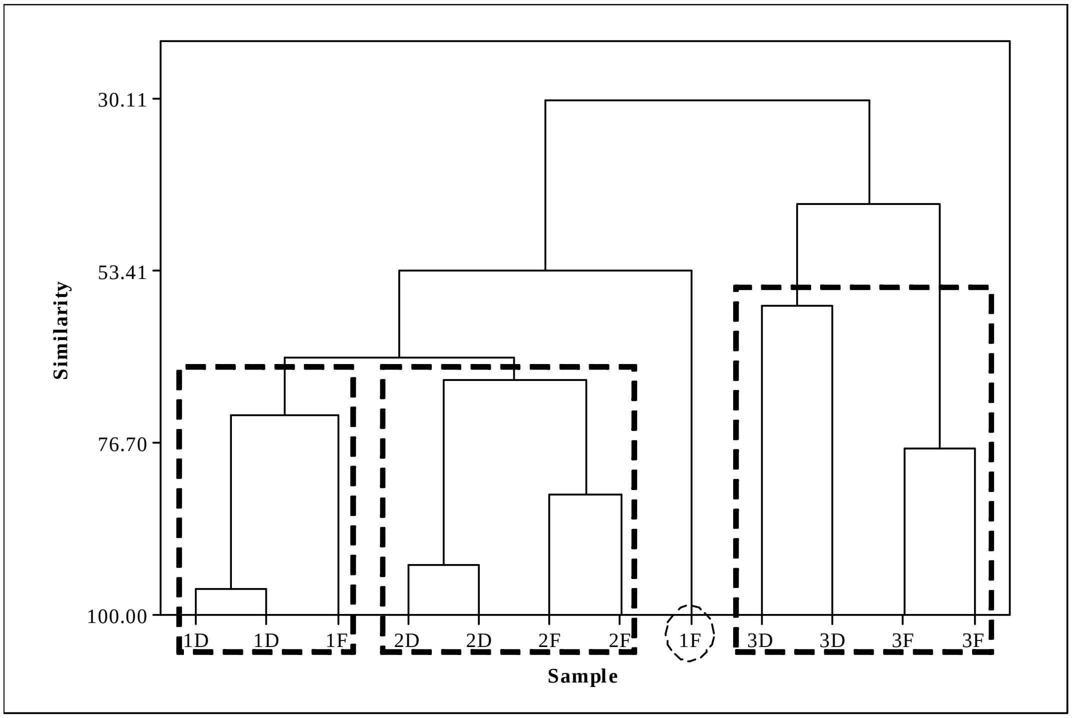


Figure 5.65: A dendogram expressed in similarity showing that the related samples prepared by direct dissolution with or without filtration are clustered in their respective groups using McQuitty linkage and Euclidean distance on standardized variables (All samples are successfully clustered except sample 1F)

5.6.1.8 Summary

The ICP-MS technique is sufficiently adequate for the quantification of trace elements present in the street doses of illicit heroin. The method was found to be simple, precise, sensitive and accurate for 18 target elements. A majority of the target analytes showed precision with an RSD $< 30\%$ despite the matrix effects. It is recommended that an initial sample weight of 30 mg for analysis be employed. Dilution may be required for concentrated analytes. As the contamination level varies highly in different brands of plastic tubes, so it is suggested that the tube be rinsed with at least two volumes of nitric acid before use. Aliquots showing particle suspensions should be filtered. Sample filtration was found to have significant effects on the ICP-MS data but it did not significantly influence the total elemental composition for sample classification. In summary, the overall ICP-MS method is suitable for the purpose of heroin profiling.

5.6.2 Statistical Validation Using Related Samples

Apart from plant uptake, the trace elements present in the illicit heroin seized from the street are most likely the combined results of contamination taking place along the route between opium purification to the packing of heroin samples. Therefore the use of this chemical data in sample classification is only confined to establishing the relationships between samples at the distribution/street level since it is not possible to determine the exact point where the elements enter the samples. Six samples (marked ‘1’ to ‘6’) showing highly different elemental compositions were selected for statistical validation. Each sample was weighed into eight different plastic tubes, totaling to 48 samples for ICP-MS analysis. Colloidal samples were also filtered like case samples. After the analysis, it was found that boron and antimony determination were difficult with certain samples. Hence, only 16 out of the 18 successful trace elements verified in Section 5.6.1 ICP-MS Method Validation were chosen for statistical validation.

5.6.2.1 Variation Associated with ICP-MS Analysis

There is a high degree of variation in the trace determination of analytes in highly complex matrices. For each sample, the RSD of the concentration of each element was calculated from 8 replicate analyses (data are obtained in ppb). Table 5.57 summarizes the RSD values obtained from the 16 trace elements found in the six unrelated samples. It was found that Ca, Cr, Mn and zinc (Zn) showed highly precise readings (RSD < 20%) in the dataset. High RSD values were consistently associated with K and Cu which showed an RSD > 100% in at least two samples. The poor RSD values were usually caused by inconsistent detection of the analytes in the samples, meaning that out of the eight analyses, the analytes were only detected once. The dataset to some extent shows a similar inference with that achieved in Section 5.6.1.4 Sample Precision, which indicates that the variation is highly affected by the sample matrix. Some of the analytes showed better RSD values in certain samples but not in others. The following section will detail the various statistical means to minimize the overall variation associated with the ICP-MS analysis.

Table 5.57: Variation in RSD (%) encountered in the dataset containing 6 batches of related samples analyzed by ICP-MS

Element	**Sample (n = 8)**					
	1	**2**	**3**	**4**	**5**	**6**
Na	2.07	8.85	14.33	14.24	3.76	73.06
Mg	7.67	48.30	59.02	55.37	5.18	3.74
Al	19.98	15.36	52.33	99.72	18.42	19.00
K	18.15	27.26	282.84	29.68	N.A.	282.84
Ca	2.43	1.44	4.40	19.41	2.23	2.25
Cr	2.22	4.37	2.74	6.52	2.00	16.92
Mn	1.60	1.34	9.60	15.85	4.42	2.47
Fe	N.A.	7.09	14.40	198.03	N.A.	11.18
Ni	13.65	29.92	51.14	52.27	32.44	9.09
Cu	N.A.	282.84	281.00	62.41	43.97	69.92
Zn	1.88	3.92	2.44	4.79	4.02	3.64
As	N.A.	N.A.	N.A.	271.80	N.A.	3.60
Se	N.A.	N.A.	76.40	187.59	N.A.	3.65
Cd	8.11	8.91	7.09	94.56	13.54	2.89
Ba	48.53	20.71	33.40	51.59	75.97	24.07
Pb	4.05	1.82	27.32	90.20	14.26	17.00

N.A. = Not applicable.

5.6.2.2 Evaluation of Pretreatment Methods

The ICP-MS data reported in ppb units (equivalent to the element relative to the selected IS) were subjected to various pretreatment methods specified in Table 5.58. The pretreated data were subsequently screened by PCA in covariance mode by decomposing the multivariate data into three principal components. Finally, the sample classification outcomes were scrutinized for the best grouping.

Table 5.58: Pretreatment methods for ICP-MS data

Pretreatment	Abbreviation	Description
No pretreatment	Ori	Each element is maintained in its ppb reading
Normalization	N	Each element is divided by the sum of elements (Similar to the concept or PRS)
Standardization	S	Each element is divided by the standard deviation calculated from that element variable
Fourth root	4R	Application of fourth root to each element
Logarithm	L	Application of logarithm to each element
Fourth root + standardization	4R + S	Each forth rooted element is divided by the standard deviation calculated from that forth rooted element variable.
Logarithm + standardization	L + S	Each logarithm pretreated element is divided by the standard deviation calculated from that logarithm pretreated element variable.
Normalization + standardization	N + S	Each normalized element is divided by the standard deviation of that normalized element variable
Normalization + fourth root	N + 4R	Application of fourth root to each normalized element
Normalization + fourth root + standardization	N + 4R + S	Application of standardization to the N + 4R data.

The respective score plots revealed that Ori, N and 4R methods were not able to segregate certain sample units of one group from the other groups. On the other hand, S, L, 4R + S, L + S, N + S and N + 4R + S showed the potential to classify the samples in to their groups but with insufficient distinction since the sample units in the groups were only widely packed. A better outcome was achieved by using N + 4R (Figure 5.66), through which the groups become more distinctive although not all the sample units are successfully clustered in their groups. Therefore, the use of N + 4R is useful to compensate for the weight difference between analyses. It is also able to moderately minimize the effect of high concentration such as Na in the dataset. According to Figure 5.66, Groups 1 and 5 showed closely packed sample units. Groups 2 and 6 respectively showed a slightly distant sample unit. Group 3 showed one relatively distant sample unit. Group 4 showed the worst clustering with three sample units being well-separated from the relatively closely packed cluster and this was also consistently observed with other pretreatment methods.

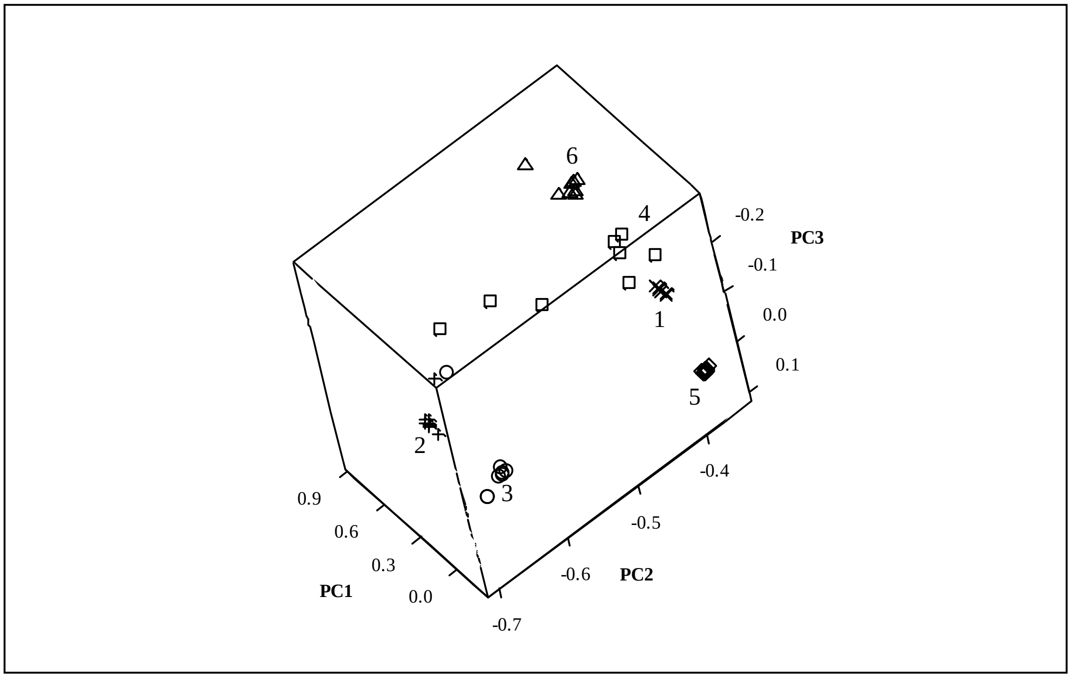


Figure 5.66: A score plot representing 16 N + 4R pretreated elemental data of 48 data points decomposed by PCA in covariance mode into three dimensions, $\%V_1 = 71.4\%$, $\%V_2 = 12.2\%$ and $\%V_3 = 10.8\%$ (The distribution shows distinct groups)

The loadings in Table 5.59 suggest that Ca, Fe, As and Se with loadings > 0.3 were associated with the first component. As and Se were associated with the second component while none of the elements were significantly associated with the third component. This also infers that the data variability becomes less significant in the third component. A total of 94.4% data variability was retained in the first three components.

Table 5.59: Loadings of the first three principal components of 16 N + 4R data of 48 samples

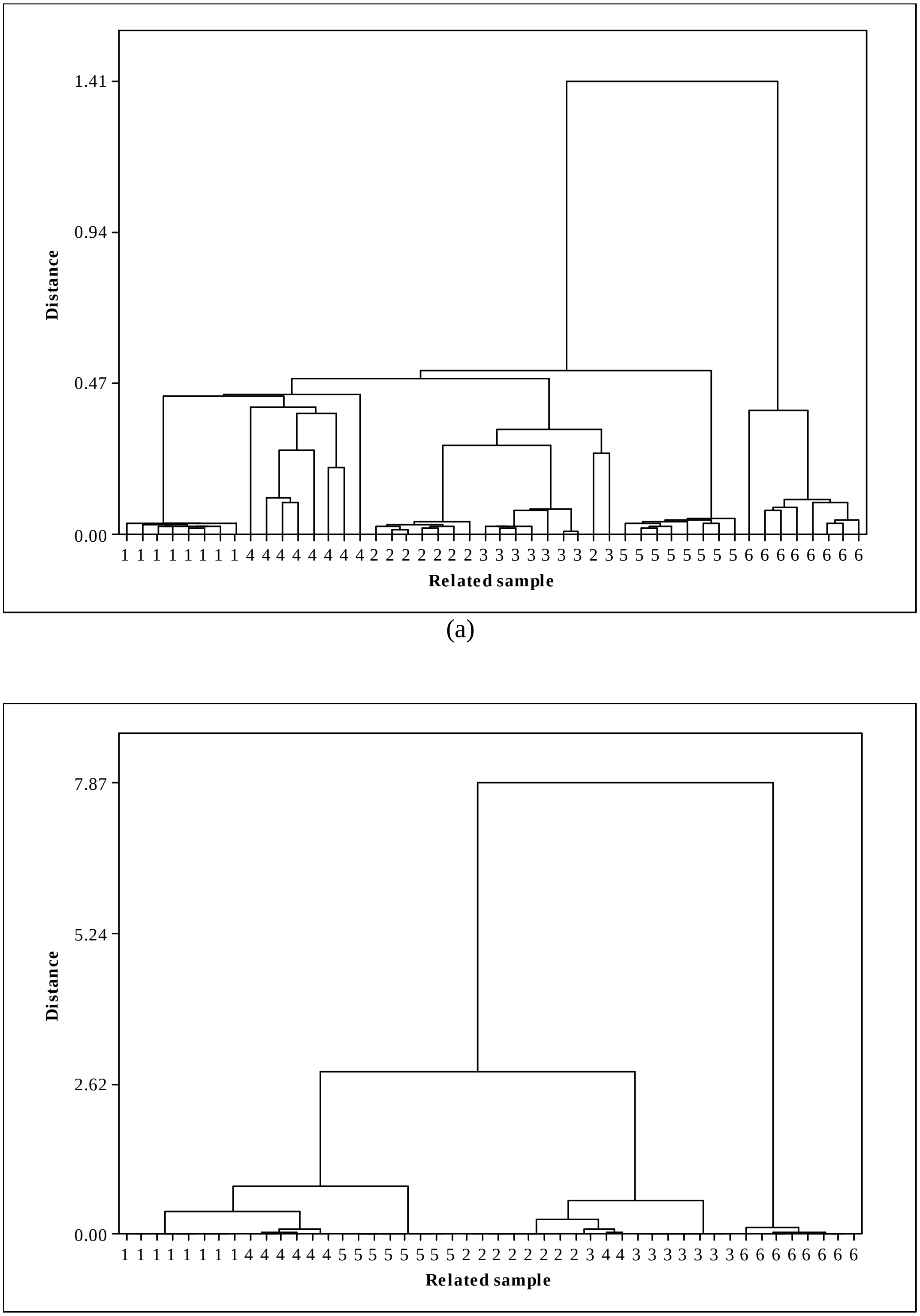
N + 4R of element	PC1	PC2	PC3
Na	-0.471	-0.152	0.056
Mg	0.260	0.039	-0.175
Al	0.048	-0.153	-0.024
K	-0.211	-0.268	-0.874
Ca	0.417	-0.312	0.151
Cr	0.031	0.038	0.061
Mn	0.069	0.046	-0.111
Fe	0.399	-0.691	0.010
Ni	0.067	-0.008	-0.076
Cu	0.081	0.131	-0.287
Zn	0.116	-0.033	-0.066
As	0.314	0.305	-0.203
Se	0.446	0.398	-0.166
Cd	0.016	-0.022	0.002
Ba	0.057	-0.125	0.016
Pb	0.008	-0.127	0.013

5.6.2.3 Evaluation of Linkages and Distance Measures

The 48 N + 4R data points were used to assess the best linkage methods and distance measures for HCA. Successful techniques should show zero or the least number of mistaken units as well as the lowest d_m value. These results and the classification outcomes generated with the ICP-MS data are presented in Table 5.60 and Figure 5.67.

Table 5.60: Number of samples erroneously clustered and the d_m value in parenthesis obtained with 48 samples analyzed by HCA

Method		Distance measure				
		Euclidean	Manhattan	Pearson	Squared Euclidean	Squared Pearson
Linkage method	**Average**	6 (12.14)	4 (9.84)	4 (18.41)	6 (2.53)	4 (5.27)
	Centroid	4 (13.84)	4 (10.44)	4 (20.61)	6 (2.26)	4 (5.33)
	Complete	6 (11.22)	4 (9.00)	5 (17.16)	6 (1.96)	5 (4.59)
	McQuitty	6 (13.06)	4 (10.05)	5 (20.13)	6 (2.68)	5 (6.23)
	Median	4 (16.34)	4 (11.04)	6 (19.05)	6 (2.84)	5 (7.22)
	Single	4 (15.71)	3 (11.70)	6 (16.32)	4 (3.70)	6 (3.44)
	Ward	4 (2.31)	4 (1.66)	4 (3.43)	4 (0.42)	4 (0.95)



(a)

(b)

Figure 5.67: Dendograms expressed in distance showing the distance relationships between 48 random case samples using (a) Single linkage and Manhattan distance and (b) Ward linkage and Squared Euclidean distance.

According to Table 5.60, none of the combinations of the linkage method and distance measure was able to give zero mistakes. Single-Manhattan (Figure 5.67(a)) is the only combination that gave the least number of mistakes (6% or 3 out of 48 samples) but its d_m value is relatively high. This indicates that the inter-group distance is very close to the distances within the groups and hence the poorer separation. Alternatively, it was decided to select the Ward-Squared Euclidean (Figure 5.67(b)) as the preferred combination since it showed a reasonably low number of mistakes (8% or 4 out 48 samples) as well as the lowest d_m value among all other combinations.

5.6.2.4 Summary

From the statistical analysis of the ICP-MS data obtained from the 6 batches of 8 related samples, both PCA and HCA revealed that N + 4R was the ideal pretreatment method for sample clustering. Both the statistical techniques were not able to cluster all the related samples under their respective batches, but by using the Ward-Squared Euclidean only 8% mistakes were made with the best discriminative power expressed as d_m were achieved with the N + 4R data in the HCA. This technique will be applied to the case samples for distribution/street level comparison.

5.6.3 Analysis of Heroin Case Samples

A total of 309 genuine heroin case samples confirmed in Task 3 were analyzed using the validated ICP-MS and statistical methods. Quantitative analysis was achieved by using a three-point calibration method and all the ICP-MS data were obtained in ppb units for 16 target elements. Only elements that were successfully detected in both the duplicate analyses were considered as being truly present.

In this subtask, polyatomic interferences could pose a problem. Hence, sample classification was assessed on the basis of the mass-to-charge (m/z) ratio represented by the selected trace elements rather than the true elements per se.

5.6.3.1 Sample Analysis

The simple direct dissolution procedure undertaken in this study is the preferred method for high throughput analysis. However, the method itself has its limitations. Using 30 mg (the gross sample weight) of illicit heroin as an initial weight was sufficient for the detection of the 16 target elements in the majority of the samples, but at this weight, 37 samples showed saturated Na which required further sample dilution or reduction of weight (e.g. 10 mg) for a second analysis. In addition, approximately 10% of the samples contained undissolved particles, and thus requiring an additional step of sample filtration to remove the particles. The particles were usually the unidentified substances (e.g. dirt) which are assumed to have been acquired from the uncontrolled environment during processing and packing.

In terms of the instrumental contamination, the blank analysis indicated that the instrument showed some degree of contamination with Na (1.4 ppb), K (4.1 ppb), Cr (0.003 ppb), Mn (0.002 ppb), Fe (5.3 ppb), As (0.1 ppb), Se (0.3 ppb), cadmium (Cd) (0.01 ppb), Ba (0.009) and Pb (0.006). Despite such contamination, the performance of the instrument was checked by a control sample and all the elements showed percent errors within ±20%. Hence, the ICP-MS data used in this study are sufficiently reliable. Furthermore, the reported value for each element was confirmed by the duplicate analysis of each sample. Also, possible interference from the interfering species was largely eliminated by checking the mass spectra or m/z value. In relation to this, the software has a function to automatically correct any possible isobaric and polyatomic overlaps. Hence, the ICP-MS data are regarded as valid for establishing the elemental profiles for the heroin samples.

5.6.3.2 Elemental Composition in Heroin Samples

From the duplicate analysis, the mean value representing the concentration of the element in each sample was computed. The mean concentrations (ppb level) of the 16 target elements found in the 309 street heroin samples are summarized in Table 5.61 (heroin column). The findings show that As was the least common element which was only present in 49% of the case samples. Other elements including Al, K, Fe, nickel (Ni), Cu, Se, Cd, Ba and Pb were frequently detected in more than 77% of the total number of samples within the instrumental detection limits. The remaining elements comprising Na, Mg, Ca, Cr, Mn and Zn were detected in all the samples.

According to Table 5.61, the standard deviation of the concentration of each element varied significantly, indicating a marked difference in the concentration between the samples. Hence, the median values instead of the mean values should be used as the latter are not reliable to evaluate the central tendencies of the data, especially when it involves a large number of zero values. The median statistics show that Na was present in extremely high levels (~8.5 ppm). The second highest was Ca (~0.9 ppm), followed by K (~43 ppb), Zn (~27 ppb), Mg (~22 ppb) and Fe (~16 ppb) in a decreasing order. Other elements were only measured in less than 10 ppb.

Trace elements in high levels represented by the third quartile (Q3) show a slightly different order. Q3 represents the level of the element at 75% position in the dataset before approaching the maximum value for the element in the dataset. It was common for Na and Ca to be found at the ppm level. This was followed by K (~93 ppb), Al (~67 ppb), Zn (~44 ppb), Fe (~38 ppb), Mg (~38 ppb) and Cr (~12 ppb). The other elements were still present at less than 10 ppb. The concentration of Al in Q3 is 7 folds of its median value. Perhaps, the instrument was unable to detect its presence since the level tended to fall below the LOD.

Although Cd was present in 77% of the samples, its level was however very low (median = 0.01 ppb, Q3 = 0.02 ppb) probably because this element is a rare element in the environment.

At this stage of analysis, the high level of Na is assumed to have come from sodium bicarbonate (which changes to sodium carbonate in hot water), a substance used to precipitate out the white heroin (Zerel *et al*., 2005). Similarly, the high level of Ca could be ascribed to the use of lime in morphine isolation (Zerel *et al*., 2005) or the addition of Ca-containing substances such as calcium bicarbonate, ascorbic acid and talcum powder to the heroin samples as thinners/fillers (Infante *et al.*, 1999). Fe, Al, Zn were probably leached from the metal containers used in opium cooking (Infante *et al.*, 1999; Bora *et al.*, 2002). Other elements could have been merely acquired from plant uptake and/or introduced as contaminants from the numerous sources involved in the chain of distribution. For instance, K and Ca are naturally high in poppy straw (Çopur, Göger, Orbey & Şener, 2005) and they could have been passed on to the final heroin products. As the samples in this study were highly cut, potential contaminants from secondary sources such as water and containers used in cutting were further investigated.

Table 5.61: Summary of elemental content (ppb) found in 309 street heroin and 103 water samples

Element	**Frequency**	**Mean**		**Standard deviation**		**Median**		**First quartile, Q1**		**Third quartile, Q3**	
		Heroin (n = 309)	**Water (n = 103)**	**Heroin (n = 309)**	**Water (n = 103)**	**Heroin**	**Water**	**Heroin**	**Water**	**Heroin**	**Water**
Na	309 (100%)	11059.00	4472.00	17465.00	3566.00	8511.00	3828.00	6262.00	1871.00	12596.00	6118.00
Mg	309 (100%)	50.09	606.60	111.40	377.30	21.89	716.10	15.32	216.30	37.86	809.00
Al	299 (97%)	45.58	817.00	67.57	3078.00	9.46	57.00	1.48	29.00	67.49	196.00
K	210 (68%)	76.65	2019.00	136.86	1260.00	42.96	1922.00	0.00	1101.00	93.37	2667.00
Ca	309 (100%)	1889.00	5941.00	14944.00	4815.00	933.00	4999.00	715.00	806.00	1276.00	9243.00
Cr	309 (100%)	10.15	1.98	3.32	7.72	9.75	0.00	7.24	0.00	11.87	0.50
Mn	309 (100%)	6.75	18.41	8.31	28.25	4.36	9.00	2.45	1.80	9.11	26.70
Fe	247 (80%)	32.07	167.80	135.12	275.10	15.75	67.20	2.89	33.50	38.48	117.20
Ni	280 (91%)	0.59	2.25	4.88	5.18	0.14	0.70	0.06	0.20	0.27	1.20
Cu	295 (95%)	1.37	120.70	2.82	585.40	0.56	2.00	0.28	0.60	1.11	4.00
Zn	309 (100%)	33.06	53.30	26.12	106.80	27.40	15.40	16.74	6.20	44.41	36.60
As	151 (49%)	0.25	1.62	1.20	1.95	0.00	1.20	0.00	0.50	0.07	1.60
Se	237 (77%)	1.11	0.33	4.93	0.24	0.15	0.30	0.04	0.20	0.30	0.50
Cd	239 (77%)	0.02	0.01	0.02	0.04	0.01	0.00	0.00	0.00	0.02	0.00
Ba	303 (98%)	1.14	39.03	2.06	91.15	0.61	10.10	0.40	5.60	1.12	16.10
Pb	305 (99%)	0.54	18.20	1.51	102.40	0.21	0.40	0.15	0.20	0.37	0.90

5.6.3.3 Potential Elements from Tap Water and Mixing Container

During the cutting process, the high purity heroin is cut with adulterants using water as a mixing agent to homogenize the sample. In addition, food dyes are also added to color the final product. The mixture is then placed in a metal container which is subjected to mild heating. Water is therefore one of the sources from which metal contaminants are introduced into the sample. Anecdotally, drinking water or piped water is always employed by a drug dealer for sample mixing. Water samples from various sources were thus investigated in this study. As indicated in Table 5.61 (water column), the median values indicate that extremely high levels of Na, K and Ca were common in the tap water, but more than 50% of the cases did not contain Cr and cadmium (Cd). Other elements were only present in trace amounts. Hence, Na, K and Ca found in the post-cut heroin were likely the sum of elements inherited from plant uptake, processing as well as from the piped water. The additive effects would cause an increase in the overall concentration levels in the street heroin. Using the mean, median, first quartile (Q1) or third quartile (Q3) as a decision-making criterion, it was found that only Na and Cr in the illicit heroin were always higher than their corresponding levels in the water while Zn and Se in the illicit heroin were higher than their corresponding levels in the water in only some cases. This offers two inferences. First, the additive effects were observed in Na but not in K and Ca because the latter two could have been diluted by the bulky adulterants to the extent that their levels became very low. Second, the large proportions of Cr, Zn and Se in the illicit heroin were likely acquired from plant uptake and processing and less likely from the piped water. However, this postulation is only a general statement and is not applicable to exceptional cases. For example, a piping system which is highly contaminated with certain metals is likely to increase the metal content in the water sample. This could explain the higher mean value of Zn in the water rather than in the illicit heroin in Table 5.61 due to this exceptional case. The same applies to the higher levels of Se in the median, Q1 and Q3. If these occurrences are known, then Zn and Se in the heroin could also be acquired from the piped water provided that their levels are sufficiently high to overcome the dilution effects.

As the real piped water and cooking utensils used by the criminals were not available, it was decided to pilot test the water directed from three in-house taps and the water stored in a rusty container in order to examine metallic contamination imparted by these sources. Three samples were taken from each of these sources. The rusty container represented an extreme condition under which the heroin samples could be prepared although in most cases they do not involve rusty containers. According to Table 5.62, the tap water shows a close agreement in the statistics with that of the 103 samples in Table 5.61. This also means that the inorganic elements in the piped water in Malaysia are very likely to fall within the elemental ranges reported in Table 5.61. Moreover, this illustrates the low temporal and spatial variation in the elemental composition since the water samples (103 water samples and 9 piped water samples) were collected at two different times (respectively late-July and early-August, 2011) from various locations. Upon testing the mean values of tap water and water from the rusty container using a 2-sample t-test to measure if the difference is significant at p-value < 0.05, it was found that in the water from the rusty container, the levels of several elements are significantly higher than those from the piped water. These elements could have been leached from the rusty container. They included Na, Al, Fe, Zn, Mn and Ba as the major contaminants and Ni, and Cu as the minor contaminants. Cr was another significant contaminant exclusively coming from the rusty container since it was absent in the piped water.

Table 5.62: Comparison of elemental content (ppb) between tap water and water from a rusty container

Element	Tap water (n = 9)	Rusty container (n = 3)	p-value for 2 sample t-test[a]	Tap water (n = 9)	Rusty container (n = 3)
		Mean		Standard deviation	
Na	3139.34	3709.04	0.001	32.04	56.43
Mg	870.82	805.75	0.152	25.27	59.30
Al	28.66	50.64	0.000	5.90	3.23
K	2610.45	2485.79	[b]0.033	30.62	41.99
Ca	9753.88	9780.12	0.911	600.76	343.74
Cr	0.00	6.98	-	0.00	0.26
Mn	33.53	64.14	0.000	4.81	1.40
Fe	328.11	4002.37	0.000	169.65	79.91
Ni	1.07	8.27	0.000	0.49	0.18
Cu	0.56	6.09	0.000	0.17	0.04
Zn	360.57	960.00	0.000	240.76	11.50
As	0.51	0.59	0.051	0.05	0.04
Se	0.10	0.06	0.487	0.12	0.06
Cd	0.13	0.10	0.627	0.16	0.01
Ba	11.26	56.72	0.000	0.38	1.46
Pb	10.36	11.65	0.807	14.77	0.34

[a] p-value < 0.05 indicates a significant difference between two groups. The variance is assumed unequal as the standard deviations of the element in two groups are apparently different. For the elements in the rusty container that were present in higher concentrations than those in the tap water, only Na, Al, Mn, Fe, Ni, Cu, Zn and Ba show significant differences.

[b] This indicates the concentration of K is significantly higher in the tap water than in the rusty container.

Based on the additional studies, it is proposed that the findings in Table 5.61 are the combined results of contamination occurring at the processing and cutting levels. High levels of Na derived from the baking soda added were further enhanced by the high level of Na from the piped water. Ca originating from lime and Fe, Al and Zn from the cooking container were not enhanced by the elements from the piped water and mixing container, as their levels were severely diluted by the presence of adulterants. Furthermore, as only a small quantity of diluted sample was analyzed in this study, hence lower amounts were detected. The low level of Cr in the illicit heroin could be specifically contributed by the metal container. The remaining elements found in the illicit heroin could be from diverse sources including water and container.

As a result, the quantitative levels of the 16 elements in highly cut samples do not establish links between samples at the source/origin and manufacturing levels. The elemental composition is a sum of elements acquired from plant uptake to packing. Therefore, clustering using these elements is only meant for sample-to-sample comparison at the distribution/street level.

5.6.3.4 Correlation between Elements

The 16 target elements were correlated with each other and the r^2 values are presented in Table 5.63. Four pairs (Mn-Ca, Fe-Ca, Fe-Mn and Se-As) were found to have an $r^2 > 0.700$, indicating that these pairs always co-exist in a linear manner. This also means that the presence of one element always leads to the presence of the other in the pair. On the other hand, 24 pairs showed negative correlations. High negatives of r^2 infer that the presence of one element tends to exclude the other in the pair. The presence of one element may also lead to the presence of the other in the pair and this is represented by a very poor positive r^2 value. As many r^2 values are close to zero (while the perfect correlation is indicated by $r^2 = 1$), the elements in the pairs are thus generally not associated with each other. This also indicates that the elements chosen in this study are mostly uncorrelated and hence the use of the 16 elements is ideal for cluster analysis. In profiling studies, one of the highly correlated variables ($r^2 > 0.9$) may be excluded because its variation can be represented by the other variable in the pair. This is preferably done when too many variables are involved for statistical analysis. However, there is no strong evidence to support the exclusion of any element as most of the r^2 values are less than 0.9 in this study. Fe-Ca and Se-As ($r^2 > 0.9$) were retained because the elements also showed low correlations with other elements.

Table 5.63: Pearson correlation coefficients, r^2 between 16 target elements found in 309 street heroin samples

	Na	**Mg**	**Al**	**K**	**Ca**	**Cr**	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Cd**	**Ba**
Mg	0.231														
Al	0.024	0.183													
K	0.169	0.305	0.157												
Ca	-0.010	0.615	0.225	0.062											
Cr	0.088	0.025	0.589	0.092	-0.002										
Mn	-0.052	0.509	0.124	0.132	0.719	0.011									
Fe	-0.006	0.628	0.338	0.095	0.977	0.154	0.702								
Ni	0.001	0.172	0.095	0.017	0.277	0.097	0.203	0.296							
Cu	0.201	0.226	0.156	0.208	0.038	-0.053	0.045	0.063	0.020						
Zn	-0.069	0.147	-0.063	-0.123	0.025	0.007	-0.043	0.053	0.046	-0.063					
As	-0.000	0.119	-0.008	-0.013	0.089	-0.067	0.124	0.102	0.040	0.102	0.073				
Se	-0.002	0.076	-0.047	-0.032	0.030	-0.108	0.071	0.034	0.017	0.074	0.105	0.986			
Cd	-0.040	0.229	0.014	0.035	0.223	-0.080	0.257	0.267	0.096	0.061	0.149	0.136	0.120		
Ba	0.063	0.152	0.063	0.165	0.053	-0.064	0.095	0.091	0.035	0.260	0.118	0.131	0.129	0.179	
Pb	0.236	0.140	-0.057	-0.057	0.098	-0.125	0.198	0.087	0.056	0.120	0.316	0.189	0.244	0.148	0.229

5.6.3.5 Classification of Heroin Case Samples by Trace Elements

The 16 trace elements of the 309 genuine heroin case samples seized from the four geographical locations were first subjected to the N + 4R pretreatment. The street level relationships between these samples were assessed by PCA (covariance mode) and HCA and the results are respectively shown in Figures 5.68 and 5.69. According to the score plot, the samples are clustered in two dense areas. Samples in the dense area are assumed to have experienced the same degree of metal contamination. A few data points (such as samples 23, 199 and others) were only remotely related and these samples are assumed to have experienced significantly different degrees of metal contamination. Similarly in the dendogram, at the similarity level = -384.46, all the case samples were clustered in three major groups, each containing approximately an equal number of samples. The three clusters could have three different contamination histories. At this level, the samples in each cluster are assumed to have undergone the same contamination history and distribution activities. Two final groups are converged at the similarity level = -1353.39. This infers that both clusters are most likely to have very dissimilar elemental compositions.

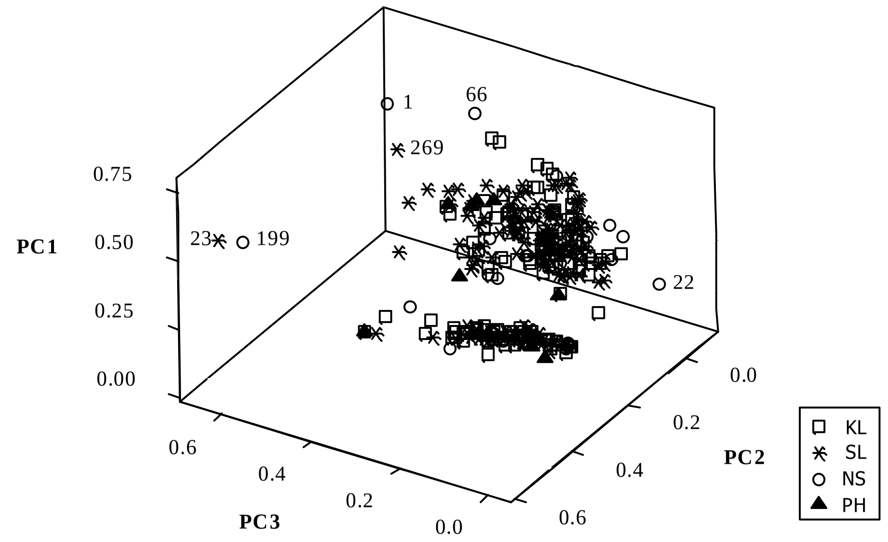


Figure 5.68: A score plot representing N + 4R pretreated elemental data obtained from 309 cases analyzed by PCA in covariance mode, $\%V_1$ = 44.5%, $\%V_2$ = 19.2% and $\%V_3$ = 13.6%

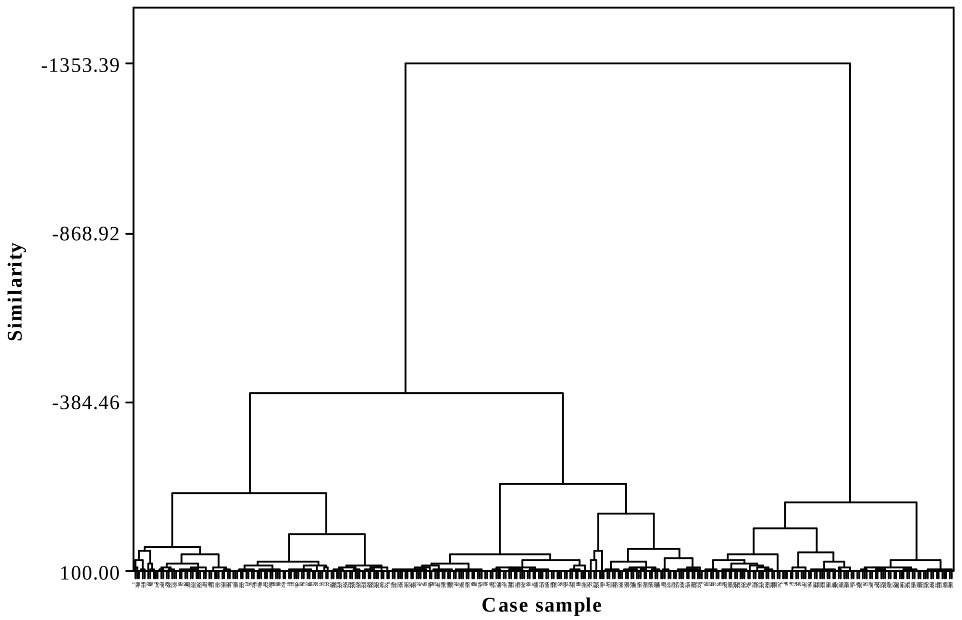


Figure 5.69: A dendogram expressed in similarity showing the relationships between 309 case samples using Ward linkage and Squared Euclidean distance

5.6.3.6 Summary

Elemental composition data from street heroin, tap water, piped water and water stored in a rusty container were compared. It was found that a number of elemental contaminants in the heroin samples could have come from water, contaminated utensils and other unreported sources. Hence, the ICP-MS data obtained from the highly cut samples were only useful for sample-to-sample comparison at the distribution/street level. In addition, PCA and HCA suggested that many case samples are closely related in at least two major clusters. The samples in each cluster are assumed to have experienced the same degree of metal contamination before they reached the street for sale.

5.7 Task 6: Data Management and Database Buildup

Five aspects of information including physical characteristics, 5 types of plastic films, 8 major components, 12 impurity peaks and 16 trace elements were collected from the 311 case samples throughout Tasks 1 to 5 (the number of case samples is subject to the feasibility in each task). This information has been statistically evaluated in their respective sections. In this final task, it aimed to store the information in a well-organized database.

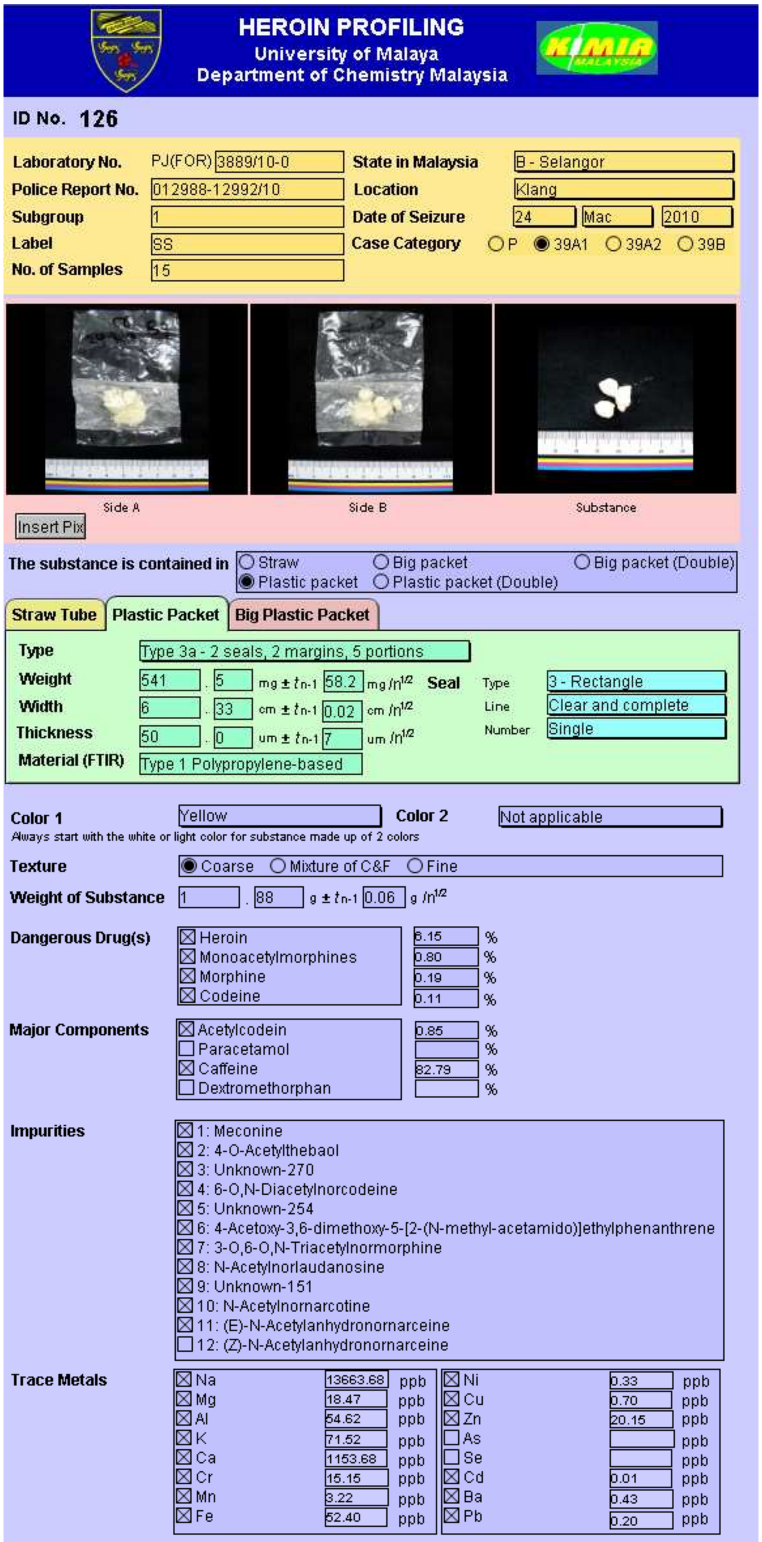
5.7.1 Development of a Database

A database was developed using Filemaker Pro 8. The above-mentioned five aspects were incorporated in the database in each datasheet which represents a profile of a single case sample (Figure 5.70). The method for data input was designed in a manner to ensure that detailed data can be preserved and yet categorical data are still traceable. An example is given as follows,

Example:

For the date, it should be 20 May 2010 in three separate fields and not in a single field such as 20 May 2010. This input method will help one track the records by day, month or year or the combination of them. If the single field is used, tracking must be forcibly done by specifying the detailed criteria.

The database enables one to search a single profile or matched profiles that share similar characteristics. By updating the information, sample classification can be effortlessly done by matching suitable characteristics. The database provides a fast gateway to retrieve relevant profiles. By tracking the samples through ‘keyword searching', rare cases can be quickly assessed. The software is user-friendly and even novices are able to use the database without much training.



HEROIN PROFILING
University of Malaya
Department of Chemistry Malaysia

ID No. 126

Laboratory No. PJ(FOR) 3889/10-0
Police Report No. 012988-12992/10
Subgroup 1
Label SS
No. of Samples 15
State in Malaysia B - Selangor
Location Klang
Date of Seizure 24 Mac 2010
Case Category ○ P ● 39A1 ○ 39A2 ○ 39B

The substance is contained in ○ Straw ○ Big packet ○ Big packet (Double) ● Plastic packet ○ Plastic packet (Double)

Type Type 3a - 2 seals, 2 margins, 5 portions
Weight 541 . 5 mg ± t_{n-1} 58.2 mg $/n^{1/2}$
Width 6 . 33 cm ± t_{n-1} 0.02 cm $/n^{1/2}$
Thickness 50 . 0 um ± t_{n-1} 7 um $/n^{1/2}$
Material (FTIR) Type 1 Polypropylene-based
Seal Type 3 - Rectangle
Line Clear and complete
Number Single

Color 1 Yellow **Color 2** Not applicable
Always start with the white or light color for substance made up of 2 colors
Texture ● Coarse ○ Mixture of C&F ○ Fine
Weight of Substance 1 . 88 g ± t_{n-1} 0.06 g $/n^{1/2}$

Dangerous Drug(s)
☒ Heroin 6.15 %
☒ Monoacetylmorphines 0.80 %
☒ Morphine 0.19 %
☒ Codeine 0.11 %

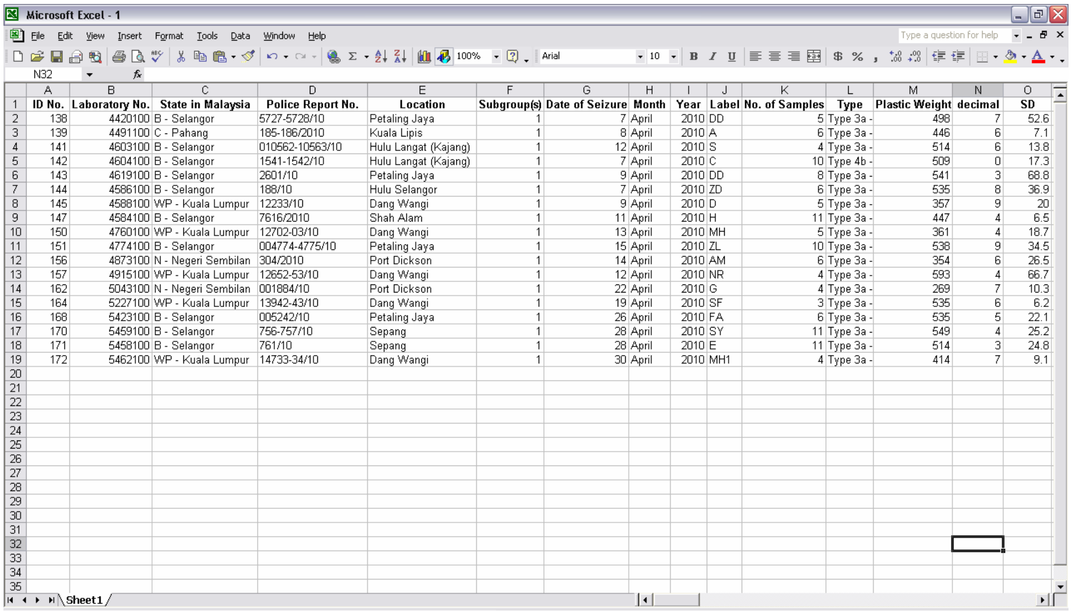
Major Components
☒ Acetylcodein 0.85 %
☐ Paracetamol %
☒ Caffeine 82.79 %
☐ Dextromethorphan %

Impurities
☒ 1: Meconine
☒ 2: 4-O-Acetylthebaol
☒ 3: Unknown-270
☒ 4: 6-O,N-Diacetylnorcodeine
☒ 5: Unknown-254
☒ 6: 4-Acetoxy-3,6-dimethoxy-5-[2-(N-methyl-acetamido)]ethylphenanthrene
☒ 7: 3-O,6-O,N-Triacetylnormorphine
☒ 8: N-Acetylnorlaudanosine
☒ 9: Unknown-151
☒ 10: N-Acetylnornarcotine
☒ 11: (E)-N-Acetylanhydronornarceine
☐ 12: (Z)-N-Acetylanhydronornarceine

Trace Metals
☒ Na 13663.68 ppb
☒ Mg 18.47 ppb
☒ Al 54.62 ppb
☒ K 71.52 ppb
☒ Ca 1153.68 ppb
☒ Cr 15.15 ppb
☒ Mn 3.22 ppb
☒ Fe 52.40 ppb
☒ Ni 0.33 ppb
☒ Cu 0.70 ppb
☒ Zn 20.15 ppb
☐ As ppb
☐ Se ppb
☒ Cd 0.01 ppb
☒ Ba 0.43 ppb
☒ Pb 0.20 ppb

Figure 5.70: A datasheet for a case sample in the database

For example, when a search starts with ‘case as possession’, ‘April’, ‘plastic packet’ and ‘off white for the substance’, 18 profiles are obtained (Figure 5.71). When the profiles are collated in an Excel spreadsheet format, the qualitative and quantitative information can be easily assessed.



ID No.	Laboratory No.	State in Malaysia	Police Report No.	Location	Subgroup(s)	Date of Seizure	Month	Year	Label	No. of Samples	Type	Plastic Weight	decimal	SD
138	4420100	B - Selangor	5727-5728/10	Petaling Jaya	1	7	April	2010	DD	5	Type 3a -	498	7	52.6
139	4491100	C - Pahang	185-186/2010	Kuala Lipis	1	8	April	2010	A	6	Type 3a -	446	6	7.1
141	4603100	B - Selangor	010562-10563/10	Hulu Langat (Kajang)	1	12	April	2010	S	4	Type 3a -	514	6	13.8
142	4604100	B - Selangor	1541-1542/10	Hulu Langat (Kajang)	1	7	April	2010	C	10	Type 4b -	509	0	17.3
143	4619100	B - Selangor	2601/10	Petaling Jaya	1	9	April	2010	DD	8	Type 3a -	541	3	68.8
144	4586100	B - Selangor	188/10	Hulu Selangor	1	7	April	2010	ZD	6	Type 3a -	535	8	36.9
145	4588100	WP - Kuala Lumpur	12233/10	Dang Wangi	1	9	April	2010	D	5	Type 3a -	357	9	20
147	4584100	B - Selangor	7616/2010	Shah Alam	1	11	April	2010	H	11	Type 3a -	447	4	6.5
150	4760100	WP - Kuala Lumpur	12702-03/10	Dang Wangi	1	13	April	2010	MH	5	Type 3a -	361	4	18.7
151	4774100	B - Selangor	004774-4775/10	Petaling Jaya	1	15	April	2010	ZL	10	Type 3a -	538	9	34.5
156	4873100	N - Negeri Sembilan	304/2010	Port Dickson	1	14	April	2010	AM	6	Type 3a -	354	6	26.5
157	4915100	WP - Kuala Lumpur	12652-53/10	Dang Wangi	1	12	April	2010	NR	4	Type 3a -	593	4	66.7
162	5043100	N - Negeri Sembilan	001884/10	Port Dickson	1	22	April	2010	G	4	Type 3a -	269	7	10.3
164	5227100	WP - Kuala Lumpur	13942-43/10	Dang Wangi	1	19	April	2010	SF	3	Type 3a -	535	6	6.2
168	5423100	B - Selangor	005242/10	Petaling Jaya	1	26	April	2010	FA	6	Type 3a -	535	5	22.1
170	5459100	B - Selangor	756-757/10	Sepang	1	28	April	2010	SY	11	Type 3a -	549	4	25.2
171	5458100	B - Selangor	761/10	Sepang	1	28	April	2010	E	11	Type 3a -	514	3	24.8
172	5462100	WP - Kuala Lumpur	14733-34/10	Dang Wangi	1	30	April	2010	MH1	4	Type 3a -	414	7	9.1

Figure 5.71: Summary of 18 matched profiles generated from the database

5.7.2 Summary

The design of the datasheet was decided based on the specific information collected from the case samples. Basically, it consists of physical and chemical data of a single case sample. With an updated database, searching becomes simple and rapid. Matched profiles can also be obtained for direct comparison.