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# Levels of Trace and Major Elements in Illicit Heroin

**ABSTRACT:** Ten elements, aluminum (Al), barium (Ba), calcium (Ca), cadmium (Cd), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), lead (Pb), and zinc (Zn) were analyzed in 44 illicit heroin samples from Southeast Anatolia, Turkey. Illicit heroin samples were dissolved in nitric acid using microwave oven and were quantified by electrothermal atomic absorption spectrometry (Cd and Pb) and inductively coupled plasma–atomic emission spectrometry (Al, Ba, Ca, Cu, Fe, Mg, Mn, and Zn). The most abundant element was calcium, 4050 to 14200 μg/g, which could be ascribed to the use of lime in the manufacturing process and/or as diluting agent. Iron (180 to 1470 μg/g), aluminum (42 to 2280 μg/g), and zinc (160 to 210 μg/g) were found at moderately high levels, possibly because of the use of metal pots in the acetic anhydride cooking process and also for storage. Cadmium and lead concentrations were at the lowest measured levels. The amounts of magnesium, manganese, barium, and copper were in the range of 100 to 800 μg/g, 3 to 17 μg/g, 4 to 30 μg/g, and 2 to 46 μg/g, respectively.

**KEYWORDS:** forensic science, heroin, element, contamination, absorption/emission spectrometry, impurity profiling

The abuse of heroin is a severe problem in the world. In order to assist the police authorities in fighting the illicit trafficking of this dangerous drug, the comparative analysis of two or more heroin samples is frequently required.

The substances found in illicit heroin are classified in four different groups by the United Nations (1). These groups are named as thinners, adulterants, impurities, and contaminants. Thinners, also called dilution agents, are pharmacologically inactive or nearly inactive substances and are added to dilute the drug. Adulterants are added substances that have moderate to significant pharmacological effect. Impurities are naturally occurring products present in opium. Contaminants are manufacturing impurities created or introduced during the synthesis of heroin. The contaminants are generally grouped as biotic or abiotic. Some microorganisms such as pollens, fungus, and bacteria are related to the first group, whereas metals belong to the second one.

A wide range of information is needed for comparative purposes. The relative amount of some components may change in heroin samples during the trafficking of the illegal drug. Generally, organic substances have been identified qualitatively and quantitatively using spectroscopic and chromatographic techniques, respectively, to find out the geographical source of heroin and to determine traffic routes (2–21).

A number of studies have dealt with the presence of metals in illicit drugs (22–30). The levels of some trace metals in heroin were determined using atomic absorption spectrometry (AAS) by Van Ormer in 1975 (22) to determine toxicological effects on users. In the last decade, an analytical pilot study on metallic contaminants in cocaine and heroin were examined by Violante et al. (23). The levels of Cd, Ca, Cu, Fe, Mn, and Zn in illicit heroin were analyzed by Infante et al. using AAS (24). It was concluded that only Cd and to a lesser extent Zn and Cu at their highest concentrations might have toxic effects to users. Also, metallic contaminants in illicit heroin and cocaine samples were examined using electrothermal atomic absorption spectrometry (ETAAS) and flame atomic emission spectrometry (FAES) by Bermejo-Barrera et al. (25–28). The results showed that two geographic origins could be established through the presence of trace elements (28). A statistical evaluation of the metalic constituents of heroin was used in the determination of geographical origin (29,30). Using hierarchical cluster analysis, K-means cluster, correlation, and principal component analysis, analyzed heroin samples by ICP-MS for 73 elements were grouped as Southeast Asian or non-Southeast Asian samples with predictive values in the range of 68 to100% by Myors et al. (29). After dichrotomizing the distribution of concentration of each of eight elements that have linear combination statistically within 39 investigated trace elements, heroin samples from Chinese and non-Chinese sources had been discriminated with a positive predictive value of 95% by Ekangaki et al. (30).

In this work, trace metals (Pb, Cd, Cu, Mn, Ba) and major metals (Ca, Fe, Zn, Mg, Al) in illicit heroin samples were analyzed. The heroin was confiscated in Southeast Anatolia, Turkey, and is assumed to be of Southwest Asian origin. The analyses were conducted in order to provide additional knowledge about the inorganic substances used as thinners, and the metallic contaminants introduced during processing, which may be useful to determine the source and the trafficking routes of the exhibits.

## Methods

The lead and cadmium measurements were carried out using Shimadzu model AA-6650 electrothermal atomic-absorption spectrometer with appropriate hollow cathode lamps. All experiments were done using pyrolytic graphite coated graphite tubes. The background corrector was a deuterium lamp. The analytical measurements were based on the absorbance peak areas.

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A Leeman Labs model sequential ICP-AES spectrometer with a standard nebulization system was used for the determination of calcium, barium, magnesium, aluminum, zinc, copper, iron, and manganese. The main operational conditions of the spectrometer and the analytical wavelengths are listed in Table 1.

Forty-four samples of illicit heroin seized in Diyarbakır (Southeast Anatolia, Turkey) between 1998 and 1999 were examined. Forty-two samples were in powdered form, and two were in lumpy form. Due to the fact that Southeast Anatolia is one of the main entrance points of heroin into Turkey, the origin of illicit heroin samples is probably Southwest Asia.

Samples of illicit heroin were digested in a Milestone model MLS 1200 Mega microwave oven equipped with an internal pressure and temperature control system. The nitric acid used was a special purity (Suprapur) from Merck. Single (for AAS) or multielement for (ICP-AES) working standard solutions of Al, Ba, Ca, Mg, Zn, Fe, Cu, and Mn were prepared from 0.1 to 1 g/L stock solutions (Merck), and ultrapure water was used for all further dilutions. All standards were acidified to obtain the proper pH.

All measurements were repeated three times for two individual digests. Typically, 0.2 to 0.4 g of heroin sample was weighed into the Teflon PFA vessel. Three milliliters of concentrated nitric acid were added and the vessel was closed tightly. The microwave time was 20 min at 650 W. Samples were cooled after the microwave treatment for approximately 30 min and then transferred into volumetric flasks and diluted to 25 mL with ultrapure water. A reagent blank solution was prepared according to the same procedure applied to the samples.

The measurement conditions were optimized on signal to background ratio. A one-point background correction in ICP-AES analysis was applied when required. Analytical results were calculated using the straight calibration graphs based on the acidified multielement standard solution.

TABLE 1—*Operating conditions of ICP-AES spectrometer and the analytical wavelengths.*

| | |
|---|---|
| Spectrometer | Echelle with a sequential detection |
| RF Power | 1 kW |
| Radio frequency | 40 MHz |
| Carrier gas flow rate | 1.0 mL/min |
| Plasma gas flow rate | 15 L $min^{-1}$ |
| Plasma observation | Radial |
| Pump uptake | 1.2 mL/min |
| Analytical wavelengths (nm) | Mn 257.690 |
| | Zn 213.856 |
| | Ba 455.403 |
| | Al 308.215 |
| | Fe 259.940 |
| | Ca 393.386 |
| | Cu 324.754 |
| | Mg 280.270 |

*Statistical Analysis*

The AAS and ICP-AES data were statistically analyzed by means of SPSS 10.0 Professional Statistics 1999. The color of the heroin and the concentration of each element in μg/g were considered as the variables for each sample. One person described the color of all of the samples at the same time. The description of the color of the heroin was brown (presumably produced by the Southeast Asian A process) and beige (presumably produced by the Southeast Asian C process) (31). After variables were defined, correlation matrix, principal component, and discriminant analysis were performed.

## Results

All illicit heroin samples contained greater or lesser amount of calcium, iron, aluminium, magnesium, barium, zinc, copper, manganese, lead, and cadmium. The minimum, maximum, and mean values of all investigated elements are given in Table 2, subdivided by color of heroin.

The element of highest concentration in the illicit heroin samples was calcium. The lowest and the highest values of calcium were 4045 and 14200 μg/g in brown heroin samples. The second highest element found in the heroin samples was iron. The highest concentration of this element, 1465 μg/g, was found in the brown heroin samples. The amounts of lead and cadmium were very low in all samples. Manganese content in the beige and brown heroin samples ranged from 3 to 17 μg/g. The aluminum level was higher in the brown heroin (the highest value was 2150 μg/g). There was no great difference between the lowest and the highest concentration of magnesium in either sets. The zinc level in the beige and brown heroin samples was also similar. Slightly higher barium concentrations were found in the beige heroin samples. The mean levels of copper in the brown heroin samples were two times that in the beige ones. The highest level of copper, 46 μg/g, was found in a brown heroin exhibit.

The correlation matrix was calculated for ten variables in beige and brown heroin samples and is given in Table 3. Strong positive correlations were observed between the pairs Fe/Al (0.801), Mg/Al (0.728), and Mn/Fe (0.711) in beige heroin samples. There was a low negative correlation between the presence of copper and zinc. On the other hand, the presence of copper is related to that of magnesium, calcium, and aluminum. The presence of lead was correlated with the presence of zinc and barium. The correlations between the pairs Fe/Al, Ca/Cu, and Pb/Zn were observed in both beige and brown illicit heroin. The presence of barium is related to that the presence of calcium and copper in brown heroin samples.

Principal component analysis was used to extract information due to the observed correlations between variables. Four components having eigenvalues greater than 1 were chosen from ten components. The total variability of these components is 72.0%.

TABLE 2—*Maximum, minimum, and mean values of metal in μg per gram of heroin.*

| | Ca | Al | Ba | Mg | Fe | Zn | Cu | Mn | Pb | Cd |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Beige Heroin Samples | | | | | |
| Min | 4800 | 25 | 2 | 100 | 125 | 30 | 2 | 4 | 5E-02 | 1E-02 |
| Max | 10400 | 485 | 28 | 790 | 980 | 210 | 16 | 17 | 3 | 15E-02 |
| Mean | 7804 | 175 | 11 | 210 | 375 | 90 | 4 | 10 | 1 | 3E-02 |
| | | | | | Brown Heroin Samples | | | | | |
| Min | 4045 | 72 | 4 | 90 | 120 | 16 | 2 | 3 | 2E-01 | 1E-02 |
| Max | 14200 | 2150 | 17 | 876 | 1465 | 176 | 46 | 17 | 1 | 15E-02 |
| Mean | 7210 | 290 | 8 | 272 | 520 | 80 | 8 | 10 | 8E-01 | 4E-02 |

TABLE 3—*Correlation matrix between pairs of elements (n = 44).*

| | Ca | Cu | Fe | Mg | Mn | Pb | Zn |
|---|---|---|---|---|---|---|---|
| | | | | BEIGE HEROIN SAMPLES | | | |
| Al | | 0.571† | 0.801† | 0.728† | 0.501* | | |
| Ba | | | | | | 0.644† | |
| Ca | | 0.426* | | | | | |
| Cu | | | | 0.429* | | | −0.428* |
| Fe | | | | 0.529† | 0.711† | | |
| Pb | | | | | | | 0.422* |
| | | | | BROWN HEROIN SAMPLES | | | |
| Al | | | 0.830** | | | | |
| Ba | 0.460* | 0.506* | | | | | |
| Ca | | 0.522* | | | 0.706† | | |
| Pb | | | | | | | 0.666* |

* 95% of significance.
† 99 % of significance.

TABLE 4—*Classification function of each metal after discriminant analysis.*

| | Variable | Ca | Mg | Al | Fe | Zn | Cu | Pb | Constant |
|---|---|---|---|---|---|---|---|---|---|
| Ca | − | | 0.0030 | 0.0011 | | | | | −1.572 |
| | + | | 0.0110 | −0.0008 | | | | | −2.129 |
| Mg | − | | | | −0.0065 | | 0.0950 | | −2.129 |
| | + | | | | −0.0100 | | 0.1990 | | −4.672 |
| Al | − | | 0.0061 | | 0.0069 | 0.0630 | | | −5.444 |
| | + | | 0.0110 | | 0.0120 | 0.0470 | | | −7.963 |
| Ba | − | 0.0570 | 0.0069 | −0.0030 | 0.0093 | 0.0570 | | 0.3500 | −5.648 |
| | + | 0.0680 | 0.0042 | 0.0017 | 0.0060 | 0.0680 | | 2.261 | −7.363 |
| Fe | − | | 0.0080 | | | | | | −1.423 |
| | + | | 0.0140 | | | | | | −2.989 |
| Zn | − | | 0.0063 | | 0.0053 | | | 1.890 | −3.426 |
| | + | | 0.0085 | | 0.0033 | | | 4.137 | −3.728 |
| Cu | − | | 0.0120 | | 0.0042 | | | | −2.379 |
| | + | | 0.0420 | | 0.0006 | | | | −5.720 |
| Mn | − | | 0.0054 | | 0.0070 | | 0.0450 | | −2.373 |
| | + | | 0.0019 | | 0.0150 | | 0.1410 | | −3.258 |
| Pb | − | | | | | 0.0460 | | | −2.272 |
| | + | | | | | 0.0680 | | | −4.238 |
| Cd | − | | 0.0075 | 0.0007 | | | | | −1.528 |
| | + | | 0.0120 | −0.0003 | | | | | −2.387 |

− below mean, + above mean.

Unrotated loadings that relate the variables to the four components given in Table 5 are the correlations of the variables with the factors. Zinc is associated with Factor 1, having 24.5% total variability (0.66). The results for Pb, Ba, and Ca are not so clear, for they have relatively high loadings on two or more factors. The correlations of Fe, Mg, and Mn with Factor 2 are 0.68, 0.68, and 0.61, respectively (21.0%). Cd dominants are in the fourth component (11.0%). The variables give low correlation with the third component (15%). Investigating a factor score plot of heroin samples defining the axes as the first two components, it can be said that no distinct separation between samples can be seen except 11, 34, and 41 (Fig. 1).

The linear discriminant analysis was applied to each metal in turn as the principal variable. The most significant results are shown in Table 4. By discriminant analysis, the variables are quan-

TABLE 5—*Principal component analysis after extraction (unrotated solution).*

| | Principal Component | | | |
|---|---|---|---|---|
| Variables | 1 | 2 | 3 | 4 |
| Al | −0.69 | 0.44 | 0.44 | 0.13 |
| Ba | 0.55 | 0.31 | 0.50 | 0.05 |
| Ca | 0.54 | 0.51 | 0.50 | −0.01 |
| Cd | 0.04 | −0.04 | −0.24 | 0.87 |
| Cu | 0.17 | 0.43 | −0.43 | 0.17 |
| Fe | −0.56 | 0.68 | 0.27 | −0.09 |
| Mg | −0.35 | 0.68 | −0.16 | 0.22 |
| Mn | 0.39 | 0.64 | −0.22 | −0.41 |
| Pb | 0.58 | 0.31 | 0.53 | 0.24 |
| Zn | 0.66 | −0.05 | 0.37 | 0.08 |

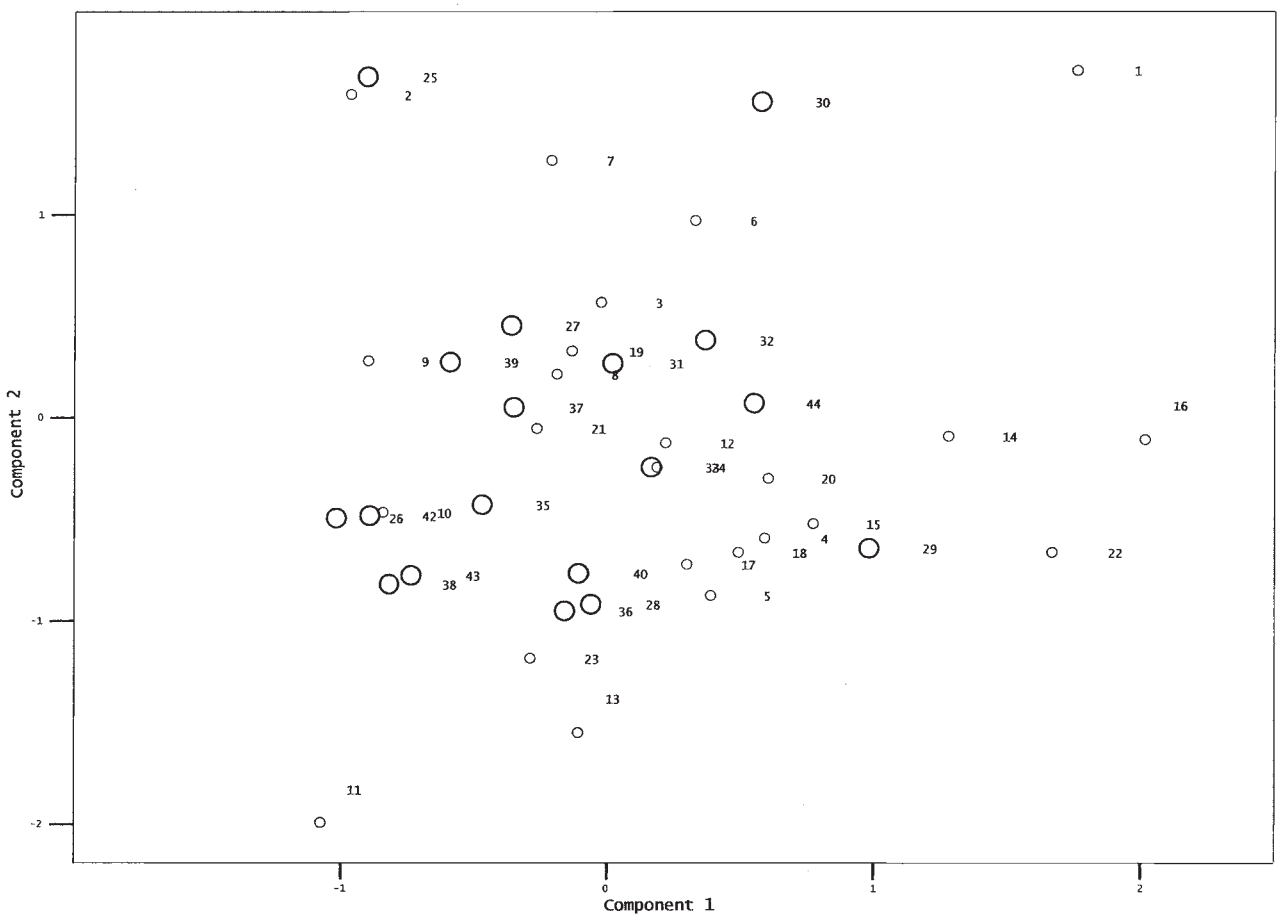


FIG. 1—*Projections of the first and second unrotated components of the scores of 44 heroin samples: o = light samples, 0 = dark samples; non-included samples, No. 34 (2,3) and No. 41 (−4;2).*

tified relatively to classify samples into suitable groups. The principal variable was above and below the mean of each metal.

The discriminant analysis based on the calcium concentration as the principal variable selects magnesium and aluminum. The magnesium content is positively related to copper and iron content. The amount of aluminum was directly related to the amount of magnesium and iron, but inversely related to the amount of zinc. Barium concentration showed positive relation with calcium, aluminum, zinc, and lead concentrations and negative relation with magnesium and iron concentrations. Iron and lead concentrations as the principal classifying variables prefer only magnesium and zinc concentrations, respectively. The manganese level gives positive relation with iron and copper levels and negative relation with magnesium level. The amount of cadmium was directly related to the amount of magnesium and inversely related to the amount of aluminum. Magnesium and lead concentrations are positively related to zinc concentration, but iron is negatively related to zinc concentration. Finally, the copper concentration was inversely related to iron and directly related to magnesium concentration.

## Discussion

The concentration ranges of the studied elements were very different in the heroin samples analyzed. The range of calcium, iron, magnesium, aluminum, and zinc concentrations were very large in both the beige and brown illicit heroin samples.

The high concentration of calcium encountered in all samples could be explained by the use of lime in the opium to morphine isolation (31) and/or merely using calcium salts (bicarbonate, chalk, talcum powder) as thinners (28).

During the synthesis of heroin, morphine is first isolated from opium poppies. Morphine is then acetylated in metallic containers to produce heroin (31). Not surprisingly, therefore, the second highest concentrated element in the illicit heroin samples was iron. The concentration of aluminum and zinc, also found as metals in reaction containers, follows the calcium and iron.

Additional negative effects in an addictís health might be due to metallic contaminants in heroin. The toxic effects of an element are measured by its dose-response relationship, where the response is the sign of an adverse effect. The toxicity effects from zinc and copper are much lower because of their easy excretion via urine. On the other hand, lead and cadmium both accumulate in the human body.

The levels of calcium, iron, manganese, cadmium, copper, and zinc in this work are much lower, but the order of element concentrations is the same as that determined by Infante et al. (24). The iron and zinc contents of this study also show similarities to literature data (8).

The existence of certain elements in heroin is related to the presence or absence of other elements. The direct relationship between the pairs of iron-aluminum, lead-zinc, and copper-calcium in both colors of heroin samples was observed. The correlation between

elements in beige heroin samples was observed more than in brown heroin.

After the application of statistical analysis to metal data, we could only say that heroin samples seem widely similar except for a few samples.

The determination of the elemental content in illicit heroin samples may be helpful in obtaining information about their origin but is probably most useful for comparative (sample/sample) analyses. The analysis of illicit drugs of known origin will be required for accurate determination of origins and/or trafficking routes.

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