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Profiling and classification of illicit heroin by ICP-MS analysis of inorganic elements

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ABSTRACT

Nineteen inorganic elements (Ag, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, Se, Sb, Th, Tl, U, V and Zn) in heroin samples were determined using inductive coupled plasma mass spectrometry (ICP-MS). After Wilcoxon–Mann–Whitney test and correlation analysis, 10 element contents (P, V, Cr, Ni, Cu, Zn, As, Se, Pb, U) and 7 element ratios (U/Ba, Ba/Pb, Cd/Mn, Co/Ni, V/Cr, P/V, Cd/V) were found to be evidently different between heroin samples from "Golden Crescent" and "Golden Triangle". Based on the data set of these 17 variables in 150 authentic heroin samples, classification of origins was successfully achieved utilizing principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA). By comparison experiment on 907 unknown samples, the developed discriminant model was proven to be consistent with the widely used organic profiling method, and meanwhile the time consumed per sample was markedly saved, which facilitates high throughput screening in routine analysis.

1. Introduction

Heroin is one of the most widely abused drugs in China. According to the Annual Report on Drug Control in China, the registered drug users reached to 2.10 million by the end of 2012, among which 1.24 million were heroin dependents [1]. The majority of the heroin consumed in China comes from "Golden Triangle" and "Golden Crescent", but the ratio of them varies every year. Therefore, heroin profiling, especially the geographical origin determination, is vital to supporting the law enforcement agency for both evidential and strategic intelligence purposes [2].

Several methods for heroin profiling have been developed by determination of the major alkaloids [3,4], acid/neutral by-products [5], and occluded solvents [6] in recent years. All these methods are based upon organic impurities, whereas another option for drug profiling is to study the inorganic composition. Elemental analysis has been used to trace the origin or production process of many illicit drugs as MDMA [7], ecstasy tablets [8,9], methamphetamine [10,11], and cannabis [12]. However, its use in the identification of heroin origin is somewhat less emphasized, as most of the studies concerned focused on the optimization of determination methods [13–18] or the variation of elemental composition of heroin samples [19–21]. Classifications of heroin seizures by elemental profile were also reported by a few works. [22–24]. R.J. Wells et al. applied ICP-MS and hierarchical cluster analysis to classify 126 individual analyses from 96 separate heroin seizures, and found that there was a close statistical correlation between seizures from the same geographical region [22]. R. Myors et al. analyzed 73 elements by ICP-MS, and several statistical procedures were adopted to differentiate 76 SEA and 20 non-SEA heroin samples [23]. Kar-Weng et al. classified 309 street heroin samples into two groups by using ICP-MS and principal component analyses (PCA) [24]. These works have provided an effective way to establish links between seizures, but rarely could the criterion of origin determination be given due to the lack of sufficient authentic samples as well as unknown samples for method validation.

This study presents a new strategy to identify heroin samples from "Golden Triangle" and "Golden Crescent" based on inorganic fingerprinting. The production of heroin contains several steps, such as poppy growth, opium harvest, morphine purification and finally acetylation of morphine. The sort and amount of the elements introduced in each step are influenced by natural environment and manufacture custom, thus ensure the possibility of origin determination by investigating the inorganic composition. In this study, a classification model for the origin determination was established and validated upon the ICP-MS analysis of 417 authentic heroin samples. Then it was applied to 907 unknown

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samples, and was proven to be reliable by comparing with results of the classic profiling method consisted of major alkaloid profiling (SIG I) and acidic & neutral components profiling (SIG II). This successful application confirmed the possibility of geographical origin determination by inorganic profile, which could be determined more quickly and easily than organic profiles.

2. Experimental

2.1. Reagents and standards

Nitric acid (65%, w/w) and hydrogen peroxide (30%, v/v), both ultrapure reagent grade, were purchased from Merck (Germany). 18.2 MΩ/cm de-ionised water (Milli-Q, USA) was used throughout.

Multi-element standard (10 mg/L of Ag, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V and Zn) was purchased from Agilent (USA). 1000 mg/L of P single-element standard was purchased from Central Iron & Steel Research Institute (China).

The element quantification was assessed using external standard method. For the determination of P, the calibration curves were 0, 1, 10, 50, 200 and 1000 μg/L and for all the other elements the concentrations of the multi-elemental standard solutions were 0, 0.001, 0.005, 0.01, 0.5, 2, 10, 50, 100 μg/L.

All polyethylene plastic bottles were rinsed with de-ionised water before use.

2.2. Sampling

417 authentic heroin samples, which consists 250 ''Golden Triangle'' samples and 167 ''Golden Crescent'' samples, were selected for the prediction modeling and model verification. All of the 167 ''Golden Crescent'' samples were from Afghanistan. 24 of them were provided by the ministry of interior of Afghanistan from the ''drug exchange program'' between China and Afghanistan. The others were provided by the Anti-smuggling Bureau of Guangzhou Custom of China. These samples were collected form seizures of body concealment cases uncovered in the airport, in which the heroin was confirmed to be from Afghanistan by both the flight information and the statement of suspects. All of the 167 ''Golden Crescent'' samples were from Myanmar. 128 of them were entry captured between the boundary of Yunnan province of China and the northern part of Myanmar. 22 of them were seized during the on-site opium field surveys of NNCC (the National Narcotics Control Commission) of China in Myanmar.

907 unknown heroin samples were selected for the comparison of the established inorganic profiling method with two organic profiling methods. These samples were randomly selected from heroin seized in different cities of China during the year of 2010–2012 and their origin information was unavailable.

A representative control sample (CT) was prepared by thorough homogenization of 15 g of one typical ''Golden Triangle'' sample and 15 g of one typical ''Golden Crescent'' sample. This mixed control sample was chosen instead of using two different control samples to save time.

2.3. Sample preparation

2.3.1. Microwave digestion

An ETHOS 1 model (Milestone) microwave digestion system equipped with an internal pressure and temperature control system was used to achieve sample digestion. Approximately 250 mg of each homogenized sample was weighed and placed inside a cleaned Teflon PFA vessel. 6 mL of 65% nitric acid and 1 mL of 30% hydrogen peroxide were added. The vessels were closed tightly and then placed in the microwave. The microwave was subjected to the following conditions: starting from the room temperature, increased to 120 °C in 5 min, and kept for 5 min, then increased to 170 °C in 5 min, kept for another 20 min. The power was set at 1200 W for the whole process. Samples were cooled after the digestion procedure and then transferred to 50 mL polyethylene plastic bottles and diluted to 50 mL with water. The end volumes of the solution were determined gravimetrically. A reagent blank solution was prepared according to the same procedure applied to the sample.

2.3.2. Ultrasonic assisted dissolution

Approximately 50 mg of each homogenized sample was weighed into a 50 mL polyethylene plastic bottle. 10 mL of 5% nitric acid solution was added with a 10 mL plastic pipette, and the end volumes of the solution were determined gravimetrically. The solution was shaken vigorously and sonicated for 10 min. Each solution was checked for the presence of particles. Another 10 min of sonication may be required to dissolve the particles. If the particles were not dissolved with further sonication, filtration was performed using a 0.45 μm filter membrane. A reagent blank solution was prepared according to the same procedure applied to the sample.

2.4. Instrumentation

An Agilent 7700 s inductively coupled plasma–mass spectrometry with ORS collision/reaction cell (CRC) was used in this study. The instrument was operated in standard He mode to remove the possible polyatomic interferences. A peristaltic pump was used for sample uptake, and a glass concentric spray chamber, and a micromist nebulizer (Agilent, USA) were used for sample solution nebulization. A 10 μg/L mixed internal standard solution (Bi, Ge, In, Li, Lu, Rh, Sc and Tb) was added on-line to the sample uptake, which allowed the automatic addition of the internal standard elements to standard, blank and sample solutions.

Typical instrumental operating conditions used were 1510 W forward power, 15 L/min plasma flow, 1.0 L/min auxiliary gas flow, 0.77 L/min carrier gas flow, 0.40 L/min makeup gas flow, respectively. A peak hopping scan mode was used with a dwell time of 1 s for As and Se, and 30 ms for other elements.

The following elements were analyzed with ICP-MS in the present study (isotope used): Ag (107), As (75), Ba (137), Cd (111), Co (59), Cr (52), Cu (63), Mn (55), Mo (95), Ni (60), P (31), Pb (208), Se (82), Sb (121), Th (232), Tl (205), U (238), V (51), Zn (66).

2.5. Organic component profiling (SIG I & SIG II)

To evaluate the developing method, two classic organic component profiling methods were employed for comparison. The first one was major alkaloid profiling (SIG I) developed by Lurie et al. [3] using capillary zone electrophoresis. Typically, 20 mg heroin equivalent of each sample was weighed into a 50 mL volumetric flask and diluted to volume with a mixture of methanol and 3.75 mM phosphate buffer (v/v = 2:8). After a 15 min sonication, the solution was filtered, and 1 μL was analyzed on an Agilent 7100 capillary electrophoresis system. The run buffer preparation and data processing were performed according to the literature [3]. The second one was acidic and neutral manufacturing impurities profiling (SIG II) developed by Morello et al. [5] using GC–MS. Typically, 45 mg morphine equivalent of each sample was placed into a centrifuge tube and dissolved in 5 mL of a mixture of petroleum ether and methylene chloride (v/v = 3:2). 4 mL sulfuric acid (2 N) was added, and after vortex and centrifugation the organic phase was isolated and dried. The residue was derivatized with MSTFA, and then analyzed on an Agilent GC–MS system (6890A GC, 5975C MS) using HP-5MS