Pak. J. Sci. Ind. Res. 2006 **49**(4) 251-255

Physical Characteristics, Inorganic Constituents and Trace Metals Determination in the Street-Vended Samples of Heroin

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(received March 21, 2005; revised August 3, 2006; accepted August 20, 2006)

Abstract. Samples of heroin collected from different parts of NWFP (North-West Frontier Province, Pakistan) were analyzed for physical characteristics, inorganic constituents (Na, K, Mg, Fe), and quantification of trace metals such as Pb, Cd, Cr, Zn, Co, Mn, Ni, Ag and Al. The analytical results of the samples were compared with those of a pure heroin sample taken as standard (marked as P). The sodium content was much higher than other inorganic adulterants in almost all the samples, which might be due to the adulteration by common salt (NaCl) and other sodium bearing materials. The calcium and magnesium contents were noted to be higher in the samples from the D. I. Khan (D-1, D-2, D-3), which is an indication of the addition of marble, dolomite and calcite as the heroin adulterants. All the samples contained trace metals in varying concentrations. Samples collected from Peshawar city were found to be highly contaminated and, therefore, contained the least quantity of heroin being 84.97% and 54.54% for samples P-2 and P-3, respectively.

Keywords: heroin determination, physical characteristics of heroin, inorganic adulterants in heroin, trace metals in heroin, heroin adulteration

Introduction

Because of high prices and no fear of detection, the adulteration in illegal drugs, particularly in heroin, is increasing day by day. Different organic and inorganic materials are mixed with heroin to fetch more profit. This situation has created an immense threat to the already deteriorated health condition of the drug addicts. One common adulteration is in the form of quinine (Inturrisi *et al.,* 1984), which also enhances the rush effects. Heroin is also mixed with milk sugar (Brien and Cohen, 1984), which gives better taste. Other adulterants include manite (a mild laxative), methadone, talcum powder, etc. Talcum powder is extremely dangerous because it does not dissolve in the blood stream. Death may result from acute reactions such as hypersensitivity, with pulmonary edema, infection, complications associated with the adulterants used, and combination of heroin with alcohol or barbiturates (Reed *et al.,* 1977), Chemically, heroin is the ester of morphine (Richard *et al.,* 1976), which is called diacetylmorphine or dimorphine. Its molecular formula is $C_{21}H_{23}NO_5$ (**C:** 68.28%, **H:** 6.28%, **N:** 3.79%, **O:** 21.66%), mol. wt. is 369.40 amu, and m.p. is 171 °C. Heroin is usually used in medicines as heroin hydrochloride. It is also found in the form of hydrochloride monohydrate (Boerner *et al.,* 1975) having the formula $C_{21}H_{24}ClNO_5.H_2O$ that forms fine crystals with m.p. of 234-244 °C. It is insoluble in ether. It is also found in the methyliodate form (Smith and Cole, 1975) having the formula $C_{22}H_{26}INO_5$ with m.p. of 252 °C. Pure heroin is a white crystalline powder with a bitter taste (Machata and Vycudlik, 1980).

Heroin is slowly absorbed from the gastrointestinal tract, which directly acts on CNS specifically affecting the pain receptor neurons. As it is lipid soluble, it directly reaches the brain and depresses the CNS in a similar way as alcohol and barbiturates, but unlike these drugs it also relieves pain (Umans *et al.,* 1982). While abuse of alcohol and barbiturates can increase belligerent behaviour by removing inhibition, heroin acts to depress aggression as well as appetite and sexual drive. It may cause skin, artery and heart diseases, loss in weight, stomach ulcer, AIDS, mental diseases, and other problems (Cohen and Stillman, 1976).

The present work was focused on the determination of physical characteristics, inorganic adulterants and trace metals in the street-vended heroin samples to check their quality and status of adulteration. Under optimized conditions the study will be useful to determine trace level concentrations of different species of illegal drugs and assessment of the quality of drugs under investigation. The studies are also expected to contribute to the awareness about drug adulteration and to minimize its abuse.

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Materials and Methods

Sampling. Street-vended heroin samples were collected from the NWFP Police Crimes Laboratories, Peshawar, Pakistan. The samples were marked as P-1, P-2, P-3, P-4, P-5 (Peshawar city), A-1, A-2, A-3 (Abbotabad city), D-1, D-2, D-3 (D. I. Khan city), N-1, N-2 (Nowshera city), S-1, S-2 (Swat city), and stored in moisture-free air tight coloured bottles. The pure sample (P) with white crystalline colour was designated as the standard. General characteristics of the samples are given in Table 1.

Reagents. AR-grade potassium chloride, sodium chloride, fuming sulfuric acid (98%), fuming nitric acid (65%), hydrochloric acid (37%), hexane (95%) pure, silica gel, formaldehyde (37%) pure, acetone (99.5%), sodium nitrate (95%) pure, methanol extra pure, and calcium sulphate were used in the studies.

Equipment and apparatus. Trace metals were determined by atomic absorption spectrophotometer model Z-8000 (Hitachi, Japan). Sodium and potassium were determined by flame photometer (Corning-410, UK). Melting points were determined with an elecrothermal melting point apparatus (Gallenkamp, England).

Procedures. Standard methods (Furman, 1962) were used for making solutions for different determinations in the heroin samples. Porcelain crucibles were soaked in chromic acid mixture and cleaned with ion-free water. The crucibles were dried at 400 °C in furnace for 3 h and then placed in a desiccator to cool down to room temperature and weighed. A weighed amount of each street-vended heroin drug was placed in the crucible and heated up to a temperature of 400 °C for 2 h in order to burn all the organic matter present in the sample. The crucible containing the non-oxidizable residue was placed in a desiccator to cool down to room temperature and then weighed. For making solutions, small volumes (2 ml) of acidic mixture (conc. sulfuric and hydrochloric acids 1:1) were added to the crucible and gently heated on an electric hot plate till the sample was dissolved. The thick acidic syrup was filtered and solutions were made with deionized water for the determination of inorganic constituents and trace metals.

Standard stock solutions of sodium and potassium were prepared form NaCl and KCl dissolved in ion-free water for the preparation of standard curves using a flame photometer. Calcium and magnesium were determined by EDTA potentiometric titration, applying standard methods (Furman, 1962). Eriochrome black T and murexide were used as indicators with buffers of pH 10.0 and pH 12.5 for the determination of calcium and magnesium, respectively.

The iron contents of the samples were determined titrimetrically with standard 0.1 N potassium dichromate solution

Table 1. Physical characteristics of the heroin samples collected from various cities in the North-West Frontier Province (NWFP) of Pakistan

Sample* number and location of collection	Colour	Loss in wt at 400 °C	Colour change	m.p. (°C)
P (pure sample)	white	90.30	yellow – light brown – red brown – black	171
P-1 (Peshawar city)	camel	66.42	camel colour – reddish brown – solid mass – black	110
P-2 (Peshawar city)	camel	65.99	camel colour – reddish brown – solid mass – black	103
P-3 (Peshawar city)	camel	60.73	camel colour – reddish brown – solid mass – black	107
P-4 (Peshawar city)	light brown	62.5	deep brown – black	140
P-5 (Peshawar city)	dark brown	61.3	deep brown – black	116
A-1 (Abbotabad city)	light brown	81.34	deep brown – blackish	105
A-2 (Abbotabad city)	dark brown	81.21	deep brown – blackish	114
A-3 (Abbotabad city)	light brown	79.53	deep brown – blackish	120
D-1 (D. I. Khan city)	camel	62.49	camel colour – dark brown – reddish brown	85
D-2 (D. I. Khan city)	fawn	4.76	no change	
D-3 (D. I. Khan city)	camel	69.48	camel colour – solid mass – black	100
N-1 (Nowshera city)	light brown	69.74	light brown – reddish – dark brown	118
N-2 (Nowshera city)	light brown	59.77	light brown – reddish – dark brown	105
S-1 (Swat city)	fawn	67.11	fawn – dark brown – black	110
S-2 (Swat city)	fawn	46.81	fawn – dark brown – black	108

* texture of all samples = powder, except A-2, which was granular; P = standard sample; m.p. = melting point

(Vogel, 1986). Potassium permanganate solution was prepared and standardized with sodium oxalate. A known volume of the sample solution was taken and the titration was stoichiometrically carried out. Keeping in view the concentration of potassium dichromate solution and its volume used, the Fe concentration in the sample solutions and its content in the respective drug, were calculated. Using prescribed procedure (Skoog and West, 1976), optimum operational conditions were attained for the determination of trace metals, such as Pb, Cd, Cr, Cu, Zn, Co, Mn, Ni, Ag and Al with flame atomic absorption spectrophotometer.

Results and Discussion

Physical characteristics of the street-vended herion samples are given in Table 1, from which it is evident that these were widely different from the pure heroin sample (P). Visual observations showed that all the samples looked different in colour, appearance and texture. The colouring was due to adulteration since pure heroin crystals are white. The observed melting points were quite different from each other indicating non-uniformity in the materials used for adulteration. Pure heroin has the melting point of 171°C (Moffat, 1986). The observed melting points were low as compared to pure heroin sample. Pure heroin is insoluble in water but soluble in chloroform and other organic solvents (Moffat, 1986; Christian, 1980). The solubility trend showed that majority of the samples had only a minimum amount of heroin, since during the dissolution process it was observed that more than 80% of the samples settled down at the bottom of the test tube or remained suspended.

Pure heroin gives black colour with Lieberman's reagent. Similarly, pure heroin gives black colour with Marquis' reagent. No uniformity was found in the resulting colours of different samples under investigation with both Lieberman's and Marquis' regents.

Thin layer chromatographic (TLC) studies were performed on all samples (Machata and Vycudlik, 1980; Cohen and Stillman, 1976). The colours developed with Marquis' reagent indicated differences in the Rf values obtained. The Rf values varied from 50 to 80 for the samples studied (Table 2). The Rf value reported in literature for pure heroin is 47 (Moffat, 1986).

The concentrations of sodium, potassium, calcium and magnesium are shown in Table 3. The sodium content was higher than potassium in all the samples. The sodium content ranged from 1.12-13.68%, whereas the standard sample (P) contained 0.62% sodium. This might be due to the presence of adulterants that had higher concentration of Na^+ ions, such as from sodium chloride (common salt). The potassium concentration ranged from 0.15-2.50%, while its concentration in the standard sample was 0.01%. The excess presence of such potassium may be due to the addition of potash alum as the adulterant. The calcium content rangeed from 0.1-1.85%, whereas the standard sample contained 0.25% calcium. The magnesium content varied from 0.02-1.05%, while the standard heroin sample contained 0.2% magnesium. The presence of higher amounts of calcium and magnesium may be due to the addition of inorganic materials like calcium carbonate, dolomite and talcum power as adulterants, due to their low price, for earning greater profits. There is also the probability of talcum as adulterant due to its soft texture as compared to limestone, marble or dolomite. A general conclusion can be further drawn that the heroin samples were adulterated with multiple adulterants.

The results of trace metals are also shown in Table 3. Iron was present in almost all the samples and its concentration was higher than the iron concentration in the standard heroin sample (P). The presence of iron may be traced back to the metallic wares in which the drugs are processed. Lead content of the samples varied from 19-1400 mg/l, which was much higher than the standard heroin sample containing 0.05 mg/l Pb. Samples from Swat city (S-1, S-2) contained highest Pb content (221-1400 mg/l), while those from Peshawar city (P-

Table 2. Observations for Marquis' and Liebermann's tests and Rf values of street-vended heroin samples

Sample number	Marquis' test	Liebermann's test	Rf
P	black	black	47
P-1	violet	black	76
P-2	deep violet	black	71
P-3	deep violet	black	80
P-4	deep violet	black	70
P-5	deep violet	black	71
A-1	deep violet	brownish black	58
A-2	deep violet	black	50
A-3	deep violet	black	66
D-1	violet	brownish black	57
D-2	soil colour	mud colour	53
D-3	blackish violet	brownish black	59
N-1	deep violet	black	78
N-2	violet	black	56
S-1	violet	brown	75
S-2	deep violet	black	66

P = pure heroin sample taken as standard

Table 3. Inorganic and trace metal composition of street-vended heroin samples

Samples number	Na	K	Ca	Mg	Fe	Pb	Cd	Cr	Cu	Zn	Co	Mn	Ni	Ag	Al	Others
	(%)				(mg/l)											(%)
P	0.62	0.01	0.25	0.20	nil	0.05	nil	nil	0.01	nil	nil	nil	nil	nil	nil	98.92
P-1	5.35	0.32	0.58	0.02	0.03	19	0.20	nil	1.80	0.02	traces	1.3	traces	0.03	1.30	93.70
P-2	13.68	0.53	0.63	0.19	0.02	35	traces	traces	1.73	0.05	0.06	1.6	0.05	0.02	0.45	84.95
P-3	14.25	0.15	0.95	0.11	0.01	38	traces	0.01	1.95	0.04	0.05	2.8	0.03	0.01	0.30	84.53
P-4	6.83	0.20	0.10	0.98	0.02	158	3.7	nil	2.5	0.01	traces	3.2	0.02	0.01	1.30	91.87
P-5	3.92	0.30	0.87	0.14	0.03	138	3.5	0.01	2.68	0.05	traces	1.5	0.03	0.02	1.20	94.74
A-1	1.12	0.25	0.53	0.34	0.01	206	1.5	0.01	3.12	0.08	0.02	1.8	0.01	traces	0.50	97.75
A-2	1.85	0.38	0.65	0.43	0.03	718	2.3	traces	0.12	0.03	0.03	0.7	traces	0.03	1.50	96.63
A-3	2.50	0.65	0.83	0.34	0.02	391	traces	nil	0.15	0.01	0.05	0.06	0.01	0.02	0.80	95.66
D-1	3.35	1.20	1.50	0.86	0.04	153	1.04	0.01	0.18	0.02	0.03	1.8	0.02	traces	0.30	93.05
D-2	2.56	1.35	1.85	1.05	0.05	234	traces	0.02	traces	0.06	traces	2.4	0.04	traces	1.85	93.14
D-3	2.83	2.50	1.52	0.93	0.02	50	traces	nil	0.10	0.02	traces	1.9	traces	traces	3.50	92.20
N-1	3.56	1.30	0.75	0.53	0.04	1400	10.4	nil	8.5	0.03	0.03	1.7	0.02	0.02	1.60	93.82
N-2	2.51	1.05	0.49	0.65	0.03	221	traces	nil	10.3	0.01	0.02	1.8	0.04	traces	1.80	94.27

P = pure heroin sample taken as standard; others = heroin plus all after organic and inorganic constituents

1, P-2, P-3, P-4, P-5) contained the least concentration of Pb (19-35 mg/l).

Cadmium was not present in the standard sample, whereas its content in the studied samples varied from traces to 1.04 mg/l. The highest Cd content was found in samples obtained from Swat city (S-1, S-2) having cadmium content of up to 10.4 mg/l. The Cr content in the samples varied from traces to 0.02 mg/l, whereas Cr was absent in the standard heroin sample. The samples collected from Nowshera city contained the highest Cr content (0.02 mg/l). The Cu content in all the samples ranged from 0.1-10.3 mg/l, whereas the standard sample contained 0.01 mg/l Cu. The samples collected from Swat city contained the highest Cu content, which was up to 10.3 mg/l. The Zn content in the samples varied from 0.01-0.08 mg/l, whereas the standard sample had no Zn content. The samples from Abbotabad city contained the highest Zn content, which was up to 0.08 mg/l. The cobalt content varied from traces to 0.02 mg/l, whereas the standard sample contained no Co content. Samples from Peshawar city contained the highest Co content (up to 0.06 mg/l). The Mn content varied from 0.06-3.2 mg/l, whereas Mn was not present in the standard sample. The samples from Abbotabad city contained the highest concentration of Mn (0.7 mg/l). The Ni content varied from traces to 0.05 mg/l, whereas the standard sample had no nickel content. The highest (0.03 mg/l) Ni was detected in samples from Peshawar city (P-1, P-2, P-3, P-4, P-5). Silver content varied from traces to 0.01 mg/l, whereas Ag was not present in the standard sample. The highest Ag content was indicated in samples from D. I. Khan and Nowshera city. The Al content varied from 0.3-3.5 mg/l, whereas the standard sample had no Al content. The highest Al content was found in samples from Nowshera city (3.5 mg/l).

The presence of all the trace metals in the samples is probably due to adulteration of the street-vended heroin samples with inorganic constituents and various mineral-bearing trace metals in their texture, which in turn increased the toxic effects of heroin.

Conclusion

On the basis of the studies undertaken, it can be concluded that pure heroin having high market price was adulterated with low priced inorganic constituents for earning greater profits. This fact has been reflected in the analyses of various samples of street-vended heroin containing such adulterants like marble, calcite, dolomite, talcum powder, common salt and sodium sulphate, thus having higher Na, K, Ca, Mg, Fe and some other trace metals in the heroin samples studied, due to the adulteration of these materials.

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