Analytical studies on illicit heroin

V. Efficacy of volatilization during heroin smoking

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Introduction

In the beginning of this century heroin was introduced into China, where it started replacing opium as a narcotic. Analogous to opium heroin was usually smoked. The heroin was brought on the market as brightly coloured pills consisting of a mixture of heroin hydrochloride and caffeine, with strychnine and/or quinine as additives.¹

In the mid-fifties in Hong Kong mostly a raw granular heroin product was smoked; it was heated on a tin foil, usually in the presence of a 'base powder' or 'daai fan'. The base powder consisted of a barbiturate which was added in order to prolong the effects of heroin and to facilitate its sublimation.²

Although nowadays heroin frequently is abused in the form of injections, smoking is still the method most frequently used, especially for beginner addicts. Heroin is sometimes smoked as cigarettes (mixed with tobacco), but inhalation of the smoke from heated aluminium foil seems to be much more popular. The latter method was originally called 'chui lung' or 'chasing the dragon', since the vapours formed looked like the tail of a dragon.² In the Netherlands this manner of abuse is called 'to Chinese'. This verb originated from the type of heroin that was encountered in the period 1970-1979, especially produced for smoking (Chinese heroin, also called 'Brown Sugar', Heroin No. 3 and Hong-Kong rocks). This type of heroin consisted of 30-40% heroin hydrochloride, 40-60% caffeine and usually also small amounts of strychnine.³⁻⁵ About 1979 new heroin types originating from South-West Asia, appeared on the West European black market. In the beginning they consisted of heroin hydrochloride, later mainly of heroin base. The heroin content was 50-80% and although caffeine sometimes was found, it was not an essential ingredient. Usually manufacturing impurities occurred in considerable amounts⁶⁷ and a wide variety of cutting agents (diluents) was reported.⁸⁹

Variations in the composition and nature of the heroin samples can be expected to have an influence on the amount of heroin available for the user. Not only the heroin content, but also the form in which heroin occurs (base or salt) are important. The base will give solubility problems for an addict who wants to prepare a solution for injection, but it is more suitable for addicts who prefer smoking. Also certain diluents may have an influence on the amount of heroin that becomes available in the smoke.

Only few data are available about the efficiency of the smoking process. It is well-known that smoking addicts use more heroin than those injecting it (Janse H, personal communication); the aluminium foils found with the addicts usually show black residues of decomposed heroin.

The brightly coloured heroin pills mentioned above, consisted of a mixture of 7 mg heroin hydrochloride, 1.75 mg strychnine nitrate and 17 mg caffeine per pill; it was reported that caffeine was found in the fumes, but no heroin.¹

A 3.835-4.644% recovery of heroin was found

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Abstract

The recovery of heroin in fumes was investigated. In the Netherlands the common mode of heroin smoking is the 'chasing the dragon' procedure: heroin is heated on an aluminium foil by a lighter and the fumes are inhaled. The efficiency of the volatilization of heroin using this procedure was studied under laboratory conditions using thin layer chromatography, gas chromatography and high pressure liquid chromatography. A considerable influence of the form (salt or base) of the heroin was found as well as strong influences of other substances that may be present in illicit heroin samples as diluents. The danger of the inhalation of fumes containing unknown pyrolysis products is mentioned and a hypothesis is given for the phenomenon of 'heroin'leucoencephalopathy that was observed in heroin smokers in Amsterdam in 1981. The types of heroin encountered in the Netherlands are discussed with regard to their suitability for smoking. when heroin hydrochloride was smoked in cigarettes, a common practice in Manchuria.¹⁰ Unfortunately very few details of the experiments were given; the analytical method was colorimetry.

Netze reported a positive influence of caffeine on the volatility of heroin hydrochloride, when heated in a TAS-oven (TAS = Thermomikro-, Abrenn-, Transfer- und Auftrage verfahren nach Stahl; thermomicro, separation, transfer and application procedure according to Stahl). In cigarettes a 10% recovery of heroin and a 15% recovery of caffeine were found. However, no influence of caffeine on the heroin recovery was observed.¹¹

Gruhzit investigated the combined use of heroin and barbiturates by Hong Kong addicts using the method of 'chasing the dragon' in order to determine if the heroin addicts also suffered from a barbiturate addiction.¹² However, no data for heroin availability were given, but for barbital 57%-95% recovery was found, depending on the heating intensity; gentle heating gave highest results.

Mo and Way studied the efficiency of heroin smoking by following urinary excretion of addicts and by simulation under laboratory conditions.¹³ For 'intravenous' addicts the average percentage of recovery of heroin (as total morphine) was 68 of the given dose, for the 'dragon chasers' 26 and for the cigarette smokers 14. The experiments under laboratory conditions consisted of heating heroin hydrochloride in a heating block, alone or mixed with barbital. Three temperatures were applied and the sublimated heroin was trapped into an acid solution during 30 min. Conclusions about heroin, monoacetylmorphine and morphine were based on a colorimetric determination of the 'total' and 'free' phenol content. Although a strong positive influence of barbital on the availability of heroin was observed, some questions remained unanswered. At 225°C a 27% recovery of 'total' heroin was found of which only 16% as unchanged heroin. At 200°C the percentage of unchanged heroin was 91, and at 260°C 50.

Cook and Brine investigated the pyrolysate of heroin hydrochloride and identified N,3,6-triacetyl-normorphine, N,6-diacetylnormorphine and O6-monoacetylmorphine.¹⁴

We found it of interest to investigate the volatilization of heroin in more detail, as many of the investigations performed so far do not very well reflect the situation concerning the types and mixtures of illicit heroin in Western Europe. Also, because of the development of several new chromatographic techniques during the last years more qualitative and quantitative information can become available. We found it also of interest to investigate the volatilization process of heroin under circumstances similar to those encountered in common practice.

Methods

TAS PROCEDURE

A TAS-oven (TAS = Thermomikro-, Abtrenn-, Transfer- und Auftrage verfahren nach Stahl; thermomicro, separation, transfer and application procedure according to Stahl) with adjustable heating was used (Desaga, Heidelberg, FRG). Of the compound or a mixture of compounds, I mg was brought into the glass tube on a small piece of aluminium foil. A stream of air, about 150 ml/min, was led through the tube, which was heated for 5 min. Compounds investigated were heroin hydrochloride, heroin base, *O6*-monoacetylmorphine hydrochloride, barbital and caffeine. Temperatures used were 175, 225, 275 and 325°C. For caffeine and barbital also 100, 125 and 150°C were investigated.

'CHASING THE DRAGON' PROCEDURE

The compound or a mixture of compounds, 10-15 mg, was heated on a piece of aluminium foil, 35×35 mm, either by means of a cigarette lighter or on the hotplate of a melting point microscope. The volatilized compounds were collected in a vertical glass reflux condenser (see Fig. 1), the lower part of which was connected to a funnel and the upper part via a tube to a water pump, giving an air flow of about 0.5 m/s through the cooler. Prior to each experiment a cotton plug (0.4 g) was brought into the upper part of the cooler.

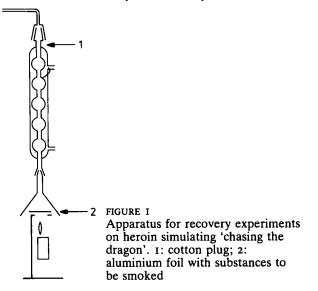
After each experiment the cooler, cotton plug and funnel were washed twice with 90 ml dichloromethane + methanol (1+1, vol/vol) and then washed twice with 2 ml of the same solvent mixture. Depending on the method applied for the analysis, either the volume was filled up to 100.0 ml or the solvents were removed completely on a water bath.

The temperatures used for the volatilization were measured by means of Thermochrom special chromatic thermometer crayons, No. 2820N (Faber-Castell, Stein bei Nürnberg, FRG).

ANALYSIS

Thin layer chromatography (TLC)

In the TAS-oven procedure vapours condensated



directly on the TLC-plate. In the 'chasing the dragon' procedure the residue, after the evaporation of the dichloromethane+methanol, was taken up in a small amount of dichloromethane+methanol, and spotted onto the TLC plate. Silicagel plates GF254 (Merck, Darmstadt, FRG) were used; the solvent system was toluene+diethylamine (85+15); visualization was achieved with UV light of 254 and 366 nm and spraying with iodoplatinate reagent.

Gas chromatography (GG)

The gas chromatograph was a Perkin Elmer (Gouda, the Netherlands) sigma 3; column temperatures were 160 and 260°C; injector and detector temperatures were 300°C; the carrier gas was nitrogen, 30 ml/min; flame ionization detector; A Perkin Elmer sigma 15 integrator and a Perkin Elmer AS 100 autosampler were used. The glass column of $2 \text{ m} \times 2 \text{ mm i.d.}$ was filled with 3% OV-17 on Chromosorb W HP, 80-100 mesh (Chrompack, Middelburg, the Netherlands).

The analyses were carried out according to the internal standard method, usually by adding 10 ml chloroform (glass distilled grade, Rathburn, Walkerburn, Scotland) (containing 0.5 mg/ml *n*-octacosane as internal standard) to the substances or the residue left after the evaporation of the eluate; for barbital determinations *n*-hexadecane was used as internal standard.

High pressure liquid chromatography (HPLC)

The HPLC equipment consisted of Perkin Elmer series 10 pumps; a Waters 441 detector (Waters Assoc., Etten-Leur, the Netherlands) at 254 nm and an SP 770 variable wavelength detector (Spectra Physics, Eindhoven, the Netherlands) at 245 nm; a Spectra Physics Labnet-AT integrator and a Perkin Elmer ISS 100B autosampler. Stainless steel columns of 25 cm \times 4.6 mm i.d. were filled with Lichrosorb Si-60-5 (prepacked, Chrompack) and RSilCN 5 µm (Alltech, Amstelveen, the Netherlands).

Eluents used were hexane+dichloromethane+methanol 75+20+5 (vol/vol, the methanol contained 0.75% vol/vol diethylamine); 1% ammonium acetate (pH 5.8)+acetonitrile+dioxane (80+10+10) vol/vol. Hexane, dichloromethane, methanol and acetonitrile were obtained from Rathburn. Diethylamine, ammonium acetate and dioxane were obtained from Merck. The analyses were carried out using the external standard method using filled loop (6 µl) injection.

REFERENCE SUBSTANCES

Most reference substances were commercially available; O6-monoacetylmorphine hydrochloride, acetylcodeine hydrochloride, normorphine and N,3,6-triacetylnormorphine were obtained as a gift from Diosynth, Apeldoorn, the Netherlands (Dr. P. Vrijhof) and from Research Triangle Institute, Research Triangle Park, North Carolina, USA (Dr. C.E. Cook).

Results and discussion

TAS-OVEN PROCEDURE

Caffeine

Caffeine evaporated easily as white fumes. At temperatures above 100°C it was detectable on the TLC plate; at 150°C most of it was sublimated onto

TABEL I

Chromatographic data for morphine, normorphine and acetylated products for thin layer chromatography (Rf values), gas chromatography (Kovats indices) and reversed-phase high pressure liquid chromatography (min)

Compound	TLC	GC	HPLC
Morphine	7	2785*	4.7
Normorphine	3	2755*	4.3
O6-Monoacetylmorphine (1)	40	2940*	5.9
N,6-Diacetylnormorphine (2)	29	3430*	8.1
N,3,6-Triacetylnormorphine (3)	55	3615	10.7
Diacetylmorphine (heroin)	62	3135	7.4

*Trimethylsilyl derivative.

the TLC plate; at 175°C a heating period of 5 min was sufficient for a complete sublimation. No charring was observed; no signs of decomposition were observed in TLC even at a temperature of 325°C.

Barbital

The behaviour of barbital was quite similar to that of caffeine.

Heroin hydrochloride

At 175°C no distinct volatilization was observed; there was no discolouration on the aluminium foil and most of the substance remained on it, although TLC showed traces of heroin, but no clear signs of decomposition products.

At 225°C a distinct volatilization was observed; after 5 min charring had taken place. The application point of the TLC plate showed a light brown spot. Examination at 254 nm showed spots of heroin and O6-monoacetylmorphine (compound 1). After heating the TLC plate at 105°C two more spots became visible by their intense blue fluorescence under UV light of 366 nm. Their identity could be established as N,3,6-triacetylnormorphine (compound 3) and N,6-diacetylnormorphine (compound 2) (Table 1).

At 275°C and 325°C an intense development of fumes was observed and a black residue remained on the aluminium foil. The application point of the TLC plate became intensely black. TLC showed heroin and increasing amounts of compounds 1, 2 and 3, but no morphine or normorphine.

The degradation pattern at 325°C was still more complex again with compounds 1, 2 and 3 as the dominant degradation products. The amounts of compounds 2 and 3 had increased so much that their spots became visible on the TLC plate under UV light of 254 nm.

In the presence of caffeine (1+1) a better volatilization was observed. Although the residues on the aluminium foil were brown, they were smaller and the starting point on the TLC plates were also considerably less dark. TLC showed again compounds 1, 2 and 3 as the main degradation products, with the largest amounts at 325°C. Now compound 1 was considerably stronger than compounds 2 and 3, in contrast with the situation when heroin hydrochloride was heated alone. The degradation pattern at 325°C was less complex with than without caffeine.

Heroin base

At 175° C most of the heroin base remained on the aluminium foil and only a slight discolouration was observed. TLC showed the presence of heroin and compound 1 in the vapour.

At 225°C heroin base volatilized almost completely, leaving a small brown residue on the foil. At higher temperatures the vapours increased. The starting points on the TLC plate showed dark spots above 225°C.

TLC showed similar results for the base as for the hydrochloride as to by-products. However, the amounts of the by-products were quite different, compounds 2 and 3 were detected only in small amounts, in contrast to compound 1, which was found in considerable quantities. At 275° C and 325° C trace amounts of morphine could be established.

In the presence of caffeine (1+1) a partial evaporation was achieved at 175° C, and complete evaporation at 225° C. At 225° C, 275° C and 325° C small light-brown residues were left on the aluminium foil. The starting points of the TLC plates were slightly discoloured. TLC showed heroin and compound 1 when a heating temperature of 175° C was applied, whereas heating at higher temperatures resulted in heroin, compound 1 and morphine. The amounts of morphine were small, those of compound 1 relatively large, those of the acetylated normorphines 2 and 3 negligible.

Acetylcodeine hydrochloride

At 175°C practically no volatilization was observed, only trace amounts of acetylcodeine were detected in TLC and some light brown colouration of the compound took place. At 225°C the volatilization increased somewhat. At 275°C it was considerable. The residues on the aluminium foil were dark brown, at 325°C black. At 325°C an intense black spot was formed on the starting point of the TLC plate. TLC showed a degradation pattern with some fluorescent spots, but no codeine.

O6-Monoacetylmorphine hydrochloride

No volatilization was observed at 175°C. At 225°C the compound left on the aluminium foil became slightly discoloured. At 275°C and 325°C substantial fumes were seen and there were only small residues left on the aluminium foil. TLC showed compound I as the main spot and three quite small fluorescent spots, one of which was morphine. There was no indication for a formation of heroin from *O*6-monoacetylmorphine.

Strychnine hydrochloride

At 175°C and 225°C no visible volatilization from the aluminium foil seemed to occur, but small amounts could be detected on the TLC plate after heating at 225°C; no clear decomposition was observed. At 275°C volatilization took place and a dark brown residue was left on the aluminium foil. At 325°C the volatilization increased parallel with the formation of dark brown TLC starting points. TLC showed a complex decomposition pattern with many fluorescent spots.

A mixture with caffeine (1+1) gave similar results, although the decomposition seemed to be less.

'CHASING THE DRAGON' PROCEDURE

Equipment and technique

The equipment used is described under *Methods*. Important parameters are the length and the diameter as well as the type of condenser. Also the adjustment of the air stream is important, since a slow air flow may result in losses of fumes near the aluminium foil, a fast one in losses at the other end of the system. The reliability of the system was checked by means of caffeine.

A sample of 10-15 mg caffeine was evaporated on the electric hotplate at 350°C. No losses of caffeine were observed at the inlet of the system, but considerable losses occurred at the outlet when a coil condenser was used; at a fast flow the caffeine particles were sucked into the pump. By means of an Allihn condenser and a cotton plug near the outlet of the cooler a yield of 95% (range 89-98%, n = 5, SD = 4%, relative SD = 4%) was obtained for caffeine. No residue was left on the aluminium foil.

Temperature

It was found by means of chromatic crayons that the temperature of the aluminium foil, when uninterruptedly heated with a lighter, rose to about 600°C in 1-2 s. Severe carbonization of organic material took place and the aluminium foil showed softening and signs of melting. Careful and interrupted heating of the foil with caffeine resulted in melting and sublimation of caffeine. It was possible to obtain a complete sublimation of caffeine at a temperature not exceeding 300°C.

Method

The heating of the aluminium foil with a lighter was carried out carefully in order to obtain the highest possible volatilization in a way that was comparable with the one used by the addicts. The heating with the lighter was interrupted or diminished as soon as fumes arose. In some cases the vapours caught alight; such experiments were left out of account. When almost all of the sample was volatilized (except for the part that charred) the heating was continued for 10 s without interruption. The 'smoking' period was strongly dependent on the compound.

The influence of the way of heating seemed to be extremely important. Even under a cautious heating great differences in the recovery were found; when the heating was performed less cautiously, considerable losses occurred. The data given as 'recoveries' represent the amounts of the compound(s) found in the smoke in percentages of the amount present in the sample heated.

In practice an addict will never be able to realize such recoveries, since his way of smoking will lead to losses of fumes. It is hard to estimate how extensive these losses are and they will differ dependent on the experience of the addict.

Analysis

Chromatographic data for morphine, normorphine and identified acetylated products are given in Table 1.

Caffeine

Caffeine melted on heating and sublimated quickly and completely within 1-1.25 min without charring. The caffeine sublimate showed no decomposition in TLC. Recovery was 88% (range 86-94%, n = 5, SD = 4%, relative SD = 4%), determined by HPLC.

Barbital

Barbital melted on heating and volatilized completely within 1 min. The average recovery was 86%(range 80-89%, n = 4, SD = 4\%, relative SD = 5\%), determined by GC.

Heroin hydrochloride

Heroin hydrochloride melted partially on heating; volatilization and discolouration occurred simultaneously. The heating period was about 2.5 min, after which a black residue was left on the aluminium foil. The weight of the residue was about a quarter of that of the heated heroin hydrochloride.

The vapours were somewhat brownish and the cotton plug in the cooler became brownish-black. Qualitative analysis of the condensate showed heroin, O6-monoacetylmorphine (compound 1), *N*,6-diacetylnormorphine (compound 2) and N,3,6-triacetylnormorphine (compound 3). Also some minor components were detected. On the TLC plate a dark starting point was formed. By means of HPLC the amount of compound 3 was determined to be about 2% of the starting material, the amount of compound 1 was about 3%; the average recovery for heroin was 17% (range 15-21%, n = 5, SD = 2%, relative SD = 15%). The recovery was thus low, probably because of a considerable carbonization and decomposition.

Heroin base

Heroin base has a melting point of 173°C, for the

hydrochloride melting points of 229-233°C (with decomposition) and 243-244°C are given.^{15 16} When heated on an aluminium foil the base melted and volatilization occurred, and only a light yellow-brown discolouration of the base was observed. Continued heating up to 2 min resulted in a dark brown or black residue.

TLC showed the same degradation products as for the hydrochloride, but a remarkable difference in the pattern was observed. Compound I was the main impurity, compound 3 was also easily detected, whereas compound 2 was found only in very small amounts. Recovery of heroin in the condensate was 62% (range 57-69\%, n = 5, SD = 5\%, relative SD = 9%).

Acetylcodeine hydrochloride

Acetylcodeine hydrochloride melted under decomposition. The melt remained liquid quite long, but gradually it became dark and gave a considerable residue; the heating period was 2.0-2.2 min. TLC showed several spots, a number of which with blue fluorescence, but no positive reaction with the iodoplatinate spray reagent. No codeine was detected. An average recovery of 24% was found by HPLC.

O6-Monoacetylmorphine hydrochloride

O6-Monoacetylmorphine occurs often in considerable amounts in 'Heroin No. 3' samples. For that reason heating experiments were carried out only in the presence of caffeine. With such a mixture (1+1) a mean recovery of 23% was found.

Strychnine nitrate/hydrochloride

On heating of strychnine nitrate heavy reddishbrown vapours developed, simultaneously with a strong carbonization. The compound did not melt, but a black cinder-like residue was left. The heating period was about 1 min. TLC showed a decomposition pattern with 15-20 mostly fluorescent spots. The part of unchanged strychnine was less than 4% of the original amount. The hydrochloride showed a strong black-colouring on heating without melting. First white and then reddish vapours developed. The heating period lasted 2.5 min and a considerable black residue remained on the aluminium foil.

A mixture of strychnine hydrochloride and caffeine (1+1) showed first a behaviour similar to that of caffeine, but slow discolouration took place and dark fumes were formed. A considerable black residue remained. The heating period was 2.0 min. Qualitative TLC showed a similar decomposition pattern as the pure hydrochloride. Quantitative analysis showed an average recovery of unchanged strychnine of 6%. In the latter smoking experiment the mean yield for caffeine was only 56%.

Heroin hydrochloride+caffeine mixtures

Mixtures of heroin hydrochloride and caffeine in

proportions of 1+1 and 1+4 were investigated. Both mixtures showed first a behaviour that resembled caffeine, but the mixtures on the aluminium foil rapidly discoloured to brown. A black residue was left with a negligible weight.

TLC of the condensate showed heroin and caffeine, together with the three degradation products mentioned before. Figure 2 shows the chromatogram obtained for heroin hydrochloride alone and for the mixture with caffeine (1+1). As can be seen, the effect on the formation of by-products is small with the exception of compound 3 which, like heroin, increases when caffeine is present.

The average recovery of heroin was 36% (range 33-47%, n = 5, SD = 9%, relative SD = 24%), respectively 51% (range 46-57%, n = 6, SD = 4%, relative SD = 8%); mean recoveries of caffeine were 74% and 80%, respectively.

Heroin hydrochloride+procaine hydrochloride The mixture of heroin hydrochloride and procaine

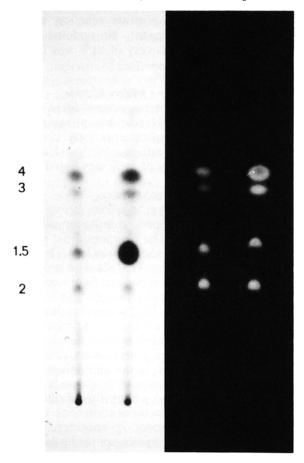


FIGURE 2

Chromatogram of condensate of heroin hydrochloride (left condensate of each pair) compared with that of heroin hydrochloride+caffeine mixture (right condensate of each pair). Left: UV 254 nm. Right: UV 366 nm. 1: O6-monoacetylmorphine; 2: N,6-diacetylnormorphine; 3:

N,3,6-triacetylnormorphine; 4: heroin; 5: caffeine

hydrochloride (1+1) melted quickly under decomposition and simultaneously a yellow colouring and the development of orange-brown vapours were observed. A voluminous black residue remained. Heating resulted in heavy decomposition. Procaine recovery was about 9%, heroin recovery about 12%.

TLC showed compound 1 as the most important decomposition product, while compound 3 was almost completely absent.

Heroin hydrochloride+barbital

The mixture of heroin hydrochloride and barbital (1+1) melted quickly to a colourless liquid and sublimation occurred. Gradually the liquid became dark and developed slightly coloured fumes. The heating period was about 2.5 min. TLC showed decomposition of heroin into compounds 1, 2 and 3, but no morphine could be detected, as was mentioned by Mo and Way.¹³ The average recovery of heroin was 33% (range 28-41%, n = 6, SD = 5%, relative SD = 14%); average barbital recovery was 51%.

Addition of caffeine or barbital to heroin hydrochloride led to an increase of the recovery of heroin, but to a decrease in the recovery of the more volatile compounds, caffeine and barbital.

Heroin base+caffeine

The 1+1 mixture of heroin and caffeine melted and volatilized quickly with only little discolouration. The melted mixture remained liquid for a long time and then suddenly charred, giving a small black residue. The heating period was about 1 min. A heroin recovery of 76% (range 68-82%, n = 5, SD = 5%, relative SD = 7%) was found; average caffeine recovery was 82%.

An illicit heroin sample

An illicit sample of South-West Asian heroin was investigated. The light brown powder contained 74% heroin base. Additionally it contained 5-6% noscapine, papaverine and acetylthebaol. On heating the sample melted immediately and became black quickly, leaving a relatively small 'shining' residue. The heating period was about 1.1 min. The heroin recovery was about 27% (calculated on sample weight, range 23-30%, n = 6, SD = 2%, relative SD = 9%), corresponding to 36% of the amount of heroin present in the sample.

Comparison of heroin compositions

A summary of the results for heroin is given in Table II. The experiments show that the efficiency of a smoking procedure is dependent both on the form of the heroin and the presence of other substances.

Smoking of pure heroin hydrochloride appears to be very inefficient; only a small part volatilizes as heroin. The compounds *O*6-monoacetylmorphine

TABLE II

Amounts of unchanged heroin found in the condensate on heating according to the procedure of 'chasing the dragon' and calculated as the percentage of heroin present in the original sample

Compound	Recovery (%)	Relative SD
Heroin hydrochloride	17	15
Heroin hydrochloride + caffeine (1+1)	36	24
Heroin hydrochloride + caffeine (1+4)	51	8
Heroin hydrochloride + barbital (1+1)	33	14
Heroin hydrochloride + procaine hydrochloride (1+1)	12	ND
Heroin base	62	9
Heroin base + caffeine (1+1)	76	7
Illicit heroin sample	36	9

(1), N,6-diacetylnormorphine (2) and N,3,6-triacetylnormorphine (3) are formed to a small extent; compound I is pharmacologically active, but less than heroin itself; little seems to be known about the activity of compounds 2 and 3.¹⁴ The major part of the heroin hydrochloride is lost by decomposition.

A remarkable increase in the efficiency is observed when heroin hydrochloride is smoked in a mixture with caffeine. A 1+1 mixture results in a doubling of the recovery, so an addition of caffeine must be considered as very rational. Also in this mixture the compounds 1, 2 and 3 are formed, but because of their small amounts they seem to be of little importance. An increase of the amount of caffeine results in higher heroin recoveries.

Addition of barbital to heroin hydrochloride gives similar results as addition of caffeine.

Addition of procaine hydrochloride, which previously was found in many samples originating from South-West Asia, does not result in higher heroin recoveries. Procaine itself is in great part decomposed.

Heroin base appears to volatilize better than the hydrochloride. During the smoking process less discolouration and charring occur when compared with the hydrochloride and less residues are found on the aluminium foil. A recovery of about 60% is found, *i.e.* about three to four times as much as for the hydrochloride.

Addition of caffeine to heroin base yields very high heroin recoveries. The caffeine recovery decreases when it is heated in a mixture with a less volatile substance. A substantial reduction is observed for the I+I mixture with heroin hydrochloride and a small reduction for the I+I mixture with heroin base. A strong reduction of the caffeine recovery is found for a mixture with strychnine hydrochloride (to 56%).

A strongly negative influence on the volatilization of heroin was observed for a South-West Asian heroin base sample; a heroin recovery of only 36% was found (against 62% for the pure base). The low result was attributed to other compounds in the sample, especially noscapine which often occurs in fairly large amounts in this type of samples. Experiments with a mixture of heroin base and noscapine base (9+1) showed a decrease of the heroin recovery to 40% (= 65% of the recovery obtained for pure heroin base). Much of the illicit heroin is prepared rather roughly; in addition to noscapine several other compounds are found, which may also have a negative influence on the volatilization of the heroin. Such an influence may also be expected of compounds added to illicit heroin as cutting agents (diluents). Heroin recoveries obtained for 1+1mixtures with frequently encountered compounds in illicit heroin samples are given in Table III. The amount of compound 1 in the condensate is also given.

Whereas addition of ascorbic acid has a destroying influence on the heroin recovery and the influence of the frequently encountered sugars is also negative, a good recovery was obtained with methaqualone. When the yield of compound I also is calculated, it is obvious that addition of relatively volatile compounds like nicotinamide, piracetam and phenazone, gives heroin recoveries in the same range as pure heroin base. Remarkable is the yield of compound I for the heroin+paracetamol mixture. Furthermore acetylparacetamol was detected in the condensate.

In the abuse of cocaine the so-called 'basing' téchnique is frequently used. The hydrochloride salt is converted to the base by addition of sodium hydrogen carbonate and water to cocaine hydrochloride. Some kind of granules are formed that are smoked in a water pipe. The base is more volatile than the hydrochloride.

TABLE III

Recovery of heroin base, when heated in a I + I mixture with frequently encountered diluents and of formed O6-monoacetylmorphine (as percentage of heroin base present in the heated sample)

Diluent	Recovery (%)			
	heroin	O6-monoacetylmorphine		
Ascorbic acid	I	II		
Cocaine base	38	14		
Colophonium	17	II		
Glucose	13	10		
Lactose	23	II		
Mannitol	25	6		
Methaqualone	55	5		
Nicotinamid	41	-		
Paracetamol	io	13 28		
Phenazone	44	6		
Piracetam	30	20		

However, this technique seems not to be applied for heroin, nevertheless we found it of interest to investigate a possible influence of sodium hydrogen carbonate and anhydrous sodium acetate on the volatilization of heroin hydrochloride. Sodium acetate was chosen because of its low melting point (58°C) and its (weakly) basic character. Sodium hydrogen carbonate had no influence on the recovery, whereas the sodium acetate increased the heroin recovery considerably (to 37%).

The results obtained show that the amounts of heroin, which become available when heroin samples are heated on an aluminium foil by means of a lighter, are strongly dependent on the nature of other substances present in the samples. Therefore, heroin addicts using the method of 'chasing the dragon' may have a different opinion on the quality of a sample than a chemist, who bases his opinion solely on the heroin content.

TOXICITY

Although some of the products formed on heating heroin samples have been identified, most of them are still unknown and their toxicity is also unknown. However, the 'traditional' combinations of compounds used so far seem not to be more toxic than heroin itself on heating on aluminium foil. New problems may arise as to the toxicity of illicit heroin samples, if used as described here, when a wide variety of new compounds are added to heroin as cutting agents.

At the beginning of 1981 several heroin addicts became seriously ill on 'heroin'-leucoencephalopathy.^{17 18} The victims were all heroin 'smokers'. From the group consisting of about 50 patients, 20 died. In spite of an extensive literature search, chemical examination of many hundreds of heroin samples and animal tests on a number of suspected heroin samples, no compound could be found responsible for the toxicity (Lousberg RJ, personal communication). The toxic compound is probably formed during the pyrolytic heating of the heroin sample and it does not need to be toxic itself. The toxicity may arise only in combination with heroin or compounds occurring in certain heroin samples.

The existence of illicit heroin samples with an incredibly high noscapine content was observed, even samples in which noscapine is the main component with only traces of heroin. In appearance such samples cannot be distinguished from common illicit heroin samples.

On heating on aluminium foil, noscapine hydrochloride appears to be partly converted to cotarnine and meconine. Pure noscapine base did not; however, together with ascorbic acid a strong formation of cotarnine was observed. Ascorbic acid is frequently encountered on the drugs scene. Cotarnine is reported to give highly toxic fumes when heated to decomposition.¹⁹

HEROIN SAMPLES AND HEROIN SMOKING

With the exception of the 'Marseilles' heroin, the first important heroin type appearing in Western Europe was the Hong-Kong No. 3, which is considered as a specific 'smoking' heroin due the high caffeine content. Because heroin was usually present as the hydrochloride, this type was soluble in water and could therefore also be used for injections. It contained small amounts of strychnine. The pharmacological effect and the danger of strychnine was questioned because of its low concentrations, usually less than 2%.²⁰ Moreover, the smoking experiments showed strychnine decomposed to a great extent.

About 1979 the early South-West Asian type of illicit heroin appeared on the black market. It contained mostly 65-80% heroin hydrochloride and in about one-third of the samples procaine hydrochloride was found. This heroin was suitable for injection because of the high heroin content and its solubility; however, heating on aluminium foil led to high decomposition and charring. This may explain why heroin smokers were not as enthusiastic about this heroin type as might be expected from its high heroin content.

Later, in the 1980s a new heroin type appeared consisting of a crude, mostly dark brown heroin base of about 50-60% purity. In addition it contained a great number of impurities, some of which in considerable amounts, like noscapine. Until 1984/ 1985 the majority of the seized illicit heroin samples were not 'cut'. The product caused some problems with respect to the solubility, but dissolution was achieved by means of ascorbic acid, citric acid or lemon juice. For a heroin smoker this heroin type should be good because of the relatively high content of heroin base. However, the amounts of impurities represented important negative factors for the heroin recovery.

In 1984 and 1985 a number of illicit heroin production units were raided in the Netherlands, where granular 'smoking heroin' was prepared. Imported highly pure heroin base was dissolved in hydrochloric acid in a rice pan, heated on a gas flame and mixed with caffeine. Traces of strychnine hydrochloride, sodium arsenilate, quinine or diazepam were also added, sometimes even dyes. On cooling a solid mass remained which was broken into granular lumps; it looked like the original 'Hong-Kong No. 3' heroin. For heroin smoking the transformation of heroin base into hydrochloride must be considered irrational.

The trend since 1984/1985 of increased mixing of heroin base with other compounds entails questions concerning their influence on the volatilization of heroin. Some compounds increase the volatilization (phenobarbital, caffeine), other compounds, especially quite volatile drugs, seem to be rather neutral, whereas a third group has a clearly negative influence on the volatilization of heroin (glucose, ascorbic acid).

Conclusion

The volatilization of heroin when heated on aluminium foil is strongly dependent on the form in which heroin occurs: base or salt. Admixed compounds have an important influence on the volatilization of heroin. Recoveries of heroin in the fumes differentiated from almost 80% for heroin base mixed with caffeine to about 1% for heroin mixed with ascorbic acid.

Caffeine has such a positive influence on the volatilization of heroin hydrochloride that it compensates within certain limits its role as diluent. Due to the circumstances mentioned above, a description of the quality of a heroin sample based on its heroin content may not agree with the opinion of a heroin smoker.

The toxicity of heroin samples on heating on an aluminium foil may increase due to compounds added as diluents.

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