

## TECHNICAL NOTE

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# GC/MS Determination of Pyrolysis Products from Diacetylmorphine and Adulterants of Street Heroin Samples\*

**ABSTRACT:** The inhalation of heroin vapors after heating on aluminium foil ("chasing the dragon") is gaining popularity nowadays among heroin users seeking to avoid the risks of parenteral drug administration. The heroin-smoking procedure was simulated under laboratory conditions by heating the samples on aluminium foil at 250 to 400°C and collecting the vapors in a condenser trap. A total of 72 pyrolysis products of diacetylmorphine, street heroin, residues from aluminium foils used to smoke street heroin, typical by-products, and adulterants were detected by gas chromatography/mass spectrometry (GC/MS). About half of these compounds could be identified. Diacetylmorphine (base and salt) undergoes substantial to complete degradation. Some typical street heroin constituents, like morphine, codeine, acetylcodeine, papaverine, and caffeine, are rather heat-stable. Other compounds, like noscapine and paracetamol, are pyrolyzed to a greater extent. The principal chemical reactions leading to the formation of pyrolysis products are desacetylation, transacetylation, N-demethylation, O-methylation, ring cleavage and oxydation.

**KEYWORDS:** forensic science, street heroin, diacetylmorphine, smoking, pyrolysis products, adulterants, GC/MS

The first heroin smoking originated in Shanghai in the 1920s, thereafter spreading across much of Eastern Asia and to the United States over the next decade (1). "Chasing the dragon" or "chinese blowing" was a later refinement of this form of heroin smoking, originating in or near Hong Kong in the 1950s, and refers to the inhalation of heroin vapors after heating the drug on aluminium foil above a flame. Subsequently, this application form was first observed in parts of Europe (e.g., the Netherlands) in the late 1970s and early 1980s and is nowadays gaining popularity among heroin users seeking to avoid the risks of parenteral drug administration (2).

However, a rare but extremely severe, often fatal neurological complication of heroin smoking is the syndrome of "toxic, spongiform leukoencephalopathy" (SLE) (2–4). The first cases of SLE were reported in 1982 from the Netherlands, where 47 heroin smokers were affected (mortality 25%) (3). Heroin contaminants in combination with cerebral hypoxia were considered responsible factors for the development of SLE. However, a definite toxin has so far not been identified (4). Recently it has been hypothesized that not constituents of street heroin vapors but primarily the release of endogenous toxins and vasogenic alterations are responsible for SLE (5).

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To our knowledge, no analytical-chemical pyrolysis studies have been performed with street heroin samples, by-products and adulterants to date. Cook and Brine (6) have analyzed pyrolysis products from diacetylmorphine hydrochloride and base and found morphines with different acetylation patterns. The aim of our study was to identify products deriving from the pyrolysis of real street heroin samples as well as common adulterants and by-products under controlled laboratory conditions by gas chromatography/mass spectrometry (GC/MS).

## Materials and Methods

### Chemicals

6-Acetylcodeine base, N-acetylnormorphine base, N,6-diacetylnormorphine base, 3-monoacetylmorphine hydrochloride, 6-monoacetylmorphine hydrochloride, and N,3,6-triacetylnormorphine base were synthesized in our laboratory; diacetylmorphine hydrochloride and base were supplied by the Swiss Federal Office of Public Health; caffeine base, 3,4-dimethoxybenzaldehyde, hydrocotarnine hydrobromide, 9-hydroxyphenanthrene, isoquinoline, 4'-methoxyacetanilide, noscapine base, N-(2-phenylethyl)-acetamide, and triacetin were provided by Fluka/Aldrich/Sigma (Buchs, Switzerland); ascorbic acid, cocaine hydrochloride, codeine base, morphine hydrochloride, paracetamol, and procaine hydrochloride were supplied by Merck (Grogg Chemicals, Bern, Switzerland); papaverine base was prepared from its hydrochloride salt provided by Merck. All solvents used were of analytical grade and purchased from Merck or Fluka. Street heroin samples and aluminium foils used for smoking were provided by heroin users in the cities of Bern and Basel.

### Pyrolysis Procedure

The apparatus described by Huizer (7) was used in a slightly modified form for all pyrolysis experiments. It consisted of a funnel, directly connected to a ball-condenser, which was kept at a constant temperature of  $-6.5^{\circ}\text{C}$  by a cooling bath (Huber K6D Power Refrigerant; Huber, Offenbach, Germany) with isopropanol-water as cooling agent. Five to 10 mg of the samples were heated at  $250^{\circ}\text{C}$  for 3 s on a piece of aluminium foil by use of a cigarette lighter. After an intermission of 5 s, the foil was heated again for 3 s. After completing ten of these heating/cooling cycles, the residue was finally heated for 10 s at  $400^{\circ}\text{C}$ . The vapor was directed through the apparatus by application of a vacuum of 900 mbar (Büchi Vacuum Controller B-168; Büchi, Flawil, Switzerland). Glass wool placed in the upper end of the ball-condenser prevented the emission of the fumes. Desorption of pyrolysis products from condenser wall and glass wool was accomplished by washing with 10 mL of methanol-dichloromethane 1:1 v/v. After concentrating under a stream of nitrogen to a volume of 1  $\mu\text{L}$ , the washing solution was membrane-filtrated and 1  $\mu\text{L}$  used for GC/MS analysis.

### Extraction of Residues from Aluminium Foils

Aluminium foils previously used for street heroin smoking were cut into pieces of about 1  $\text{cm}^2$ , extracted with 10 mL of methanol-dichloromethane 1:1 v/v for 5 min, and 1  $\mu\text{L}$  of the membrane-filtrated solutions used for GC/MS analysis.

### GC/MS Analysis

The GC/MS system consisted of an HP 5890A Series II GC with electronic pressure control, an HP 7673A autosampler, an HP 5972 mass selective detector (MSD) operated in the full scan mode ( $m/z$  28–550), and an HP Vectra 486/66 MX computer with HP 5895A Chemstation software. Chromatographic separation was achieved on a J&W Scientific DB-5 MS capillary column, 25 m by 0.2 mm ID, 0.33  $\mu\text{m}$  film, and helium at  $0.5 \text{ mL min}^{-1}$  ( $30.2 \text{ cm s}^{-1}$  at 139 kPa) as carrier gas. The oven temperature was initially held 1 min at  $85^{\circ}\text{C}$ , then increased to  $200^{\circ}\text{C}$  at a rate of  $8^{\circ} \text{ min}^{-1}$ , further increased to  $310^{\circ}\text{C}$  at  $6^{\circ} \text{ min}^{-1}$ , and held at  $310^{\circ}\text{C}$  for 10 min. The injector and transfer line temperature were set at 250 and  $280^{\circ}\text{C}$ , respectively. The injector was operated in the splitless mode. Peak identification in the total ion chromatograms (TIC) was achieved mainly by comparison of retention times and mass spectral data of standards or when not available by comparing the mass spectra with those of online accessible MS databases (Pfleger, Maurer, Weber; NIST 1998, MassLib PC version V8.6-E).

### Results and Discussion

A total of 72 pyrolysis products of street heroin, residues from aluminium foils used to smoke street heroin, typical by-products, and adulterants were detected by GC/MS. About half of these compounds (summarized in Table 1) could be identified by standards and/or comparison with mass spectra databases. The principal chemical reactions leading to the formation of pyrolysis products are desacetylation, transacetylation, N-demethylation, O-methylation, ring cleavage, and oxydation.

Only about 30% of unchanged diacetylmorphine is recovered when pyrolyzing its hydrochloride salt under controlled laboratory conditions (see Table 1). Diacetylmorphine as part of street heroin undergoes almost complete degradation (up to 99%), with 6-monoacetylmorphine, N,6-diacetylnormorphine, N,3,6-triacetyl-

TABLE 1—Pyrolysis products of street heroin, by-products, adulterants, and residues from aluminium foils used for heroin smoking.

Sample	Degradation [%]	Pyrolysis Products
Diacetylmorphine base	30	6-MAM <sup>1</sup> , DMNM, 3-MAM, DANM, M, TANM
Diacetylmorphine hydrochloride	70	6-MAM, DANM, TANM, DAP, ANM, 3-MAM, PEA, IQ, ACOD, DMNM, HP
6-Monoacetylmorphine	10	n.d.
Morphine	< 5	n.d.
6-Acetylcodeine	20	ANC, COD, DAC, DNC, DTH
Papaverine	30	HDIQ, DMB
Noscapine <sup>2</sup>	> 95	MC, HCOT
	< 5	n.d.
Procaine	50	n.d. <sup>3</sup>
Paracetamol	0 <sup>4</sup>	MA, AA
Caffeine	0	
Street heroin <sup>5</sup>	98 <sup>6</sup>	6-MAM, 3-MAM, ACOD, M, COD, TB, PAP, NOS, MC, HCOT, PAR, MA, AA, CAF, PROC
Residues from used aluminium foils		DAM, 6-MAM, ACOD, PAP, MC, HCOT, TB, TA, PAR, MA, AA, CAF, COC

<sup>1</sup> Abbreviations: 4'-acetoxyacetanilide (AA), 6-acetylcodeine (ACOD); N-acetylnorcodeine (ANC); N-acetylnormorphine (ANM); caffeine (CAF); cocaine (COC); codeine (COD); 1,10-diacetoxyphenanthrene (DAP); N,3-diacetyl-6-O-methylnormorphine (DMNM); diacetylmorphine (DAM); N,6-diacetylnorcodeine (DNC); N,6-diacetylnormorphine (DANM); 6,7-didehydroacetylcodeine (DAC); 7,8-didehydrothebaine (DTH); 3,4-dimethoxybenzaldehyde (DMB); 1-((4-hydroxy-3-methoxyphenyl)-methyl)-6,7-dimethoxyisoquinoline (HDIQ); hydrocotarnine (HCOT); 9-hydroxyphenanthrene (HP); isoquinoline (IQ); meconine (MC); 4'-methoxyacetanilide (MA); 3-monoacetylmorphine (3-MAM); 6-monoacetylmorphine (6-MAM); morphine (M); noscapine (NOS); papaverine (PAP); paracetamol (PAR); N-(2-phenylethyl)-acetamide (PEA); procaine (PROC); thebaol (TB); triacetin (TA); N,3,6-triacetylnormorphine (TANM).

<sup>2</sup> With and without addition of ascorbic acid.

<sup>3</sup> Not identified.

<sup>4</sup> Degradation only in mixture.

<sup>5</sup> Composition: DAM, PAP, NOS, PAR, CAF, PROC.

<sup>6</sup> Degradation of diacetylmorphine.

normorphine, 1,10-diacetoxy-phenanthrene, and N-acetylnormorphine as main thermal decomposition products. On the other hand, diacetylmorphine base is rather stable (only 30% pyrolysis). Apparently, the by-products and adulterants of street heroin strongly increase the pyrolysis rate.

6-Monoacetylmorphine and morphine itself were found to be stable to very stable. A low degradation rate was also measured for acetylcodeine, an impurity of manufacture present in amounts of 1 to 5% in most street heroin samples (unpublished data). We suggest that thermal demethylation and ring cleavage of the native opium alkaloid papaverine leads to the formation of 1-((4-hydroxy-3-methoxyphenyl)-methyl)-6,7-dimethoxyisoquinoline and 3,4-dimethoxy-benzaldehyde, two further compounds identified in the total ion chromatograms (TIC) of street heroin and papaverine pyrolysates.

Noscapine, another genuine opium alkaloid present in most street heroin samples, was extensively decomposed by heating, primarily to meconine (70%) and hydrocotarnine (5%). It has been postulated that cotarnine is released from heated noscapine in the

presence of ascorbic acid, which then forms highly toxic vapors through further thermal decomposition (7,8). This hypothesis could not be confirmed with our pyrolysis experiments. Caffeine and paracetamol were found to be very heat-resistant, whereas the major part of procaine, a less common heroin adulterant, was thermally decomposed to not further identified compounds.

Figure 1 shows the TIC of a street heroin sample with a composition typically found in Switzerland in the year of 2000 after pyrolysis under laboratory conditions. Abundant constituents are desacetylation products of diacetylmorphine (6-monoacetylmorphine), opium alkaloids in unchanged (papaverine), acetylated

(acetylcodeine) or decomposed form (meconine, hydrocotarnine), and adulterants (paracetamol, caffeine, procaine), some also accompanied by its degradation product (4'-acetoxyacetanilide). A fairly good correlation can be seen by comparing the TIC profiles of a pyrolyzed street heroin sample and a residue from an aluminium foil used to smoke street heroin (Fig. 2). Although the spectrum of thermal degradation products is slightly less complex, all major constituents found in the pyrolysates of street heroin samples can be detected, too. This shows that a realistic simulation of the "chasing the dragon" heroin application technique can be achieved under experimental laboratory conditions. The concomi-

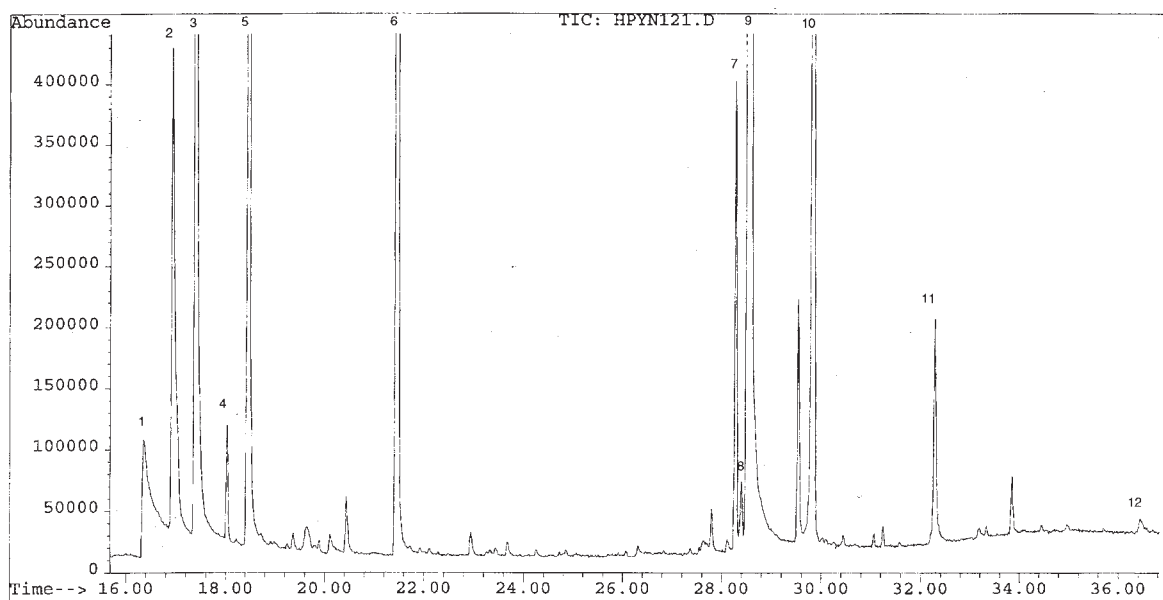


FIG. 1—Total ion chromatogram (TIC) of a pyrolyzed street heroin sample. Peak numbering: (1) PAR; (2) MC; (3) AA; (4) HCOT; (5) CAF; (6) PROC; (7) ACOD; (8) 3-MAM; (9) 6-MAM; (10) DAM; (11) PAP; (12) NOS. For abbreviations see Table 1.

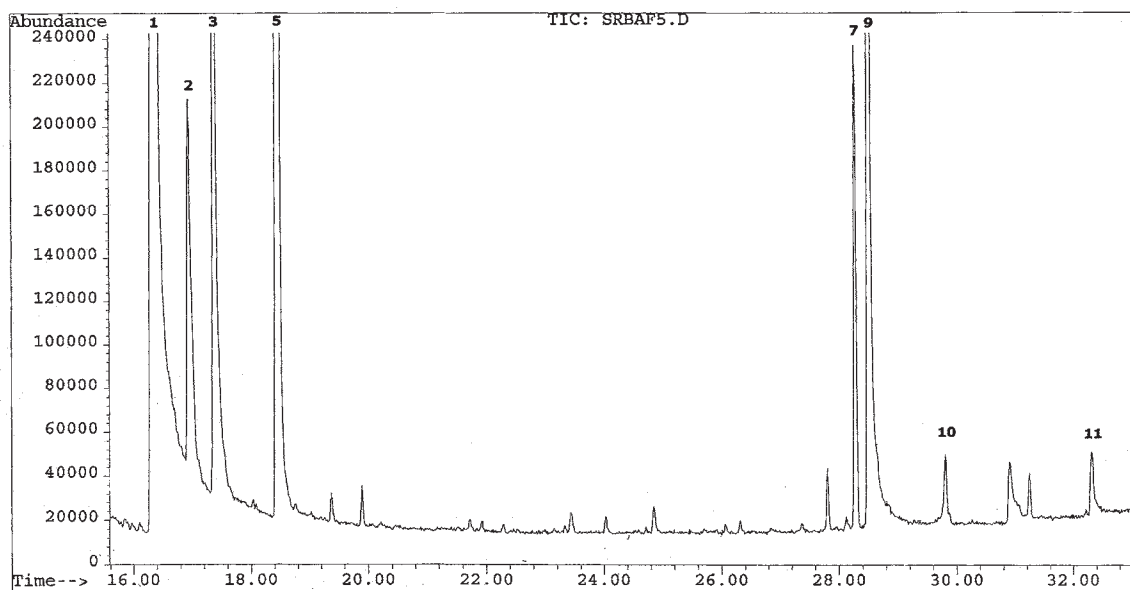


FIG. 2—Total ion chromatogram (TIC) of a residue from an aluminium foil used to smoke street heroin. For peak numbering see Fig. 1.

tant presence of cocaine on used aluminium foils indicates that multi-drug use is still popular.

### Conclusion

Our study shows the chemical complexity of pyrolytic decomposition of street heroin constituents, which is mainly the result of reactive radicals formation (9) and oxydation. Although only half of the detected pyrolysis products could be identified by GC/MS, our data can be useful to design and perform toxicological studies for the elucidation of the principle(s) causing SLE. According to two general toxicological databases (10,11), none of the identified pyrolysis products seems to be neurotoxic. However, it has to be taken into account that the described mode of heroin application is very rarely used in animal studies and only limited toxicological information is currently available. Therefore, in addition to smoking studies with animals, the (retrospective) screening of clinical, toxicological, and pathological data from heroin-smoking related intoxication cases is necessary to clarify the postulated link between "chasing the dragon" and SLE.

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