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# QUALITATIVE ANALYSIS OF EVIDENCE REGARDING HEROIN AND IMPURITIES FOR THE PURPOSES OF FORENSIC MEDICINE (FOR THE PERIOD 2000-2012)

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*Abstract* - **The use of chemical substances affecting the human psyche is as old as human history. Drug abuse is a problem which can be examined from many aspects - medical, legal, social, criminological, etc. The heart of the problem is the spread of drugs and related damage to young people, at the expense of material interests of the people involved in the system of distribution. In Bulgaria in the years after 1989 drug problem became a current issue. This work describes the results from the analysis of objects collected as evidence at crime scenes in cases of deaths of drug addicts or drug intake by living persons. The samples, after liquid / liquid extraction or directly dissolved in methanol, were analyzed by using GC with NPD detector and composition of the mixture was determined by comparison of retention times of the individual components using standard substances. After 2012, mass spectrometric identification was used. Substances and impurities, established in "street" heroin and other evidence for a period of 12 years, are summarized here. The following substances and narcotic opium alkaloids were found in most of the examined objects: acetyl codeine, 6- mono acetyl morphine, caffeine, heroin, papaverine, noscapine (narcotine), morphine and impurities: phenobarbital, diazepam, paracetamol.**

***Keywords:*** **heroin, impurities of heroine, drug, evidence.**

## I. INTRODUCTION

The use of chemical substances affecting the human psyche is as old as human history. Nowadays mass production, distribution and abuse of psychoactive substances, as well as their diversity and negative effects on society, represent a severe problem worldwide with a nature of pandemic [2,4, 6, 15].

The prevalence of heroin and its manner of use give grounds for a study of the objects used in such drug abuse – the syringes and others, presenting evidence in intravenous type of application of heroin [5, 18, 19].

The specificity of the use of injectable heroin includes pre-cooked heroin powder in lids or spoons and preparing the syringe [3,17]. Getting into a vein addicts aspirate blood which makes the solution isotonic (pH=7) and isothermal.

**Aim** of this work is to identify the composition of the evidence - "doses" in syringes, lids, spoons and compare it with "dose" of heroin powder. For this purpose, the method of gas chromatography with NPD and MS detector was used.

## II. MATERIALS AND METHODS

**Heroin.** Heroin was prepared in 1874 by Charles Right [6] in the hospital "St Merry", London. First evidences of using it as a drug are from 1910. The way of absorption of drugs evolved with the introduction of injection intake. In 1853 Scottish physicist Alexander Hood discovered the syringe – the tool that made possible the intravenous absorption of morphine and heroin, and at the same time the effect of dose was higher.

The content of the "street heroin" is divided into four main groups [16], as follows:

1. Opium alkaloids: morphine, codeine, noscapine, papaverine, thebaine.
2. Synthetic opiate alkaloids: 6-monoacetylmorphine (6-MAM), diacetylmorphine-heroin, acetylcodeine.
3. Solvents: caffeine, quinine, sugar, talcum.
4. Substituent: methadone, cocaine, ephedrine [13].

Opium alkaloids as morphine, codeine, noscapine (narcotine), papaverine, thebaine go along with heroin and are produced during the synthesis [7, 9, 12, 14]. For the same reason 6-MAM, diacetylmorphine, acetylcodeine are found as well. The other chemicals - alkaloids and medicines are deliberately added [8, 10, 11, 14].

On the street doses are called "one unit", "couples" and "threes" depending on the quantity of the drug.

On Figure 1 is presented a single dose of heroin (one unit). The special way of folding is shown sequentially in Figures 1a, 1b and 1c. It was found that all doses are folded in a similar manner, which is a marker for heroin.

A total number of 44 evidence materials (3 single doses of heroin and 41 syringes) were tested using gas chromatography with nitrogen-phosphorus detector (GC - NPD). After about 10 years of storage another 17 evidence objects (5 lids, 3 spoons and 9 syringes) were tested using gas chromatography with mass spectrometry detector (GC -

MS). The studied objects contain a solution prepared by cooking heroin with citric acid. Prepared this way, heroin is converted into a salt of tartaric acid (tartrate). During the application of heroin addicts suction blood from a vein in the syringe, thereby making the solution isotonic, isohydric and isothermal. In all studied syringes was detected blood or traces of blood, except for insulin syringes (3 pcs).

Figure 2 shows the syringes (volume 2 ml) and insulin syringes (volume 1 ml) prepared for use. They were collected from crime scenes as evidence.


**1a**


**1b**


**1c**

**Figure 1. a,b,c. A single dose of heroin (unit) with a special way of folding**

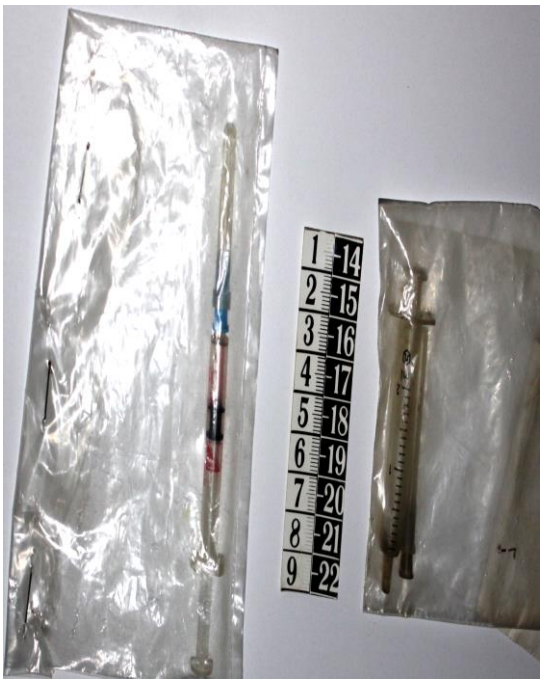

**Figure 2. Syringes (volume 2 ml) and insulin syringes (volume 1 ml), collected from a crime scene**

**Standard solutions:**

• omnopon - analgesic drug, comprising morphine, codeine, noscapine (narcotine), papaverine, thebaine, and morphine hydrochloride (drug, Sofarma PCL, Sofia, 20 mg/mL),

• morphine hydrochloride, ampoule, (Sofharma PCL, Sofia)

**Other reagents and chemicals**: chloroform, methanol, isopropanol, all for GC grade, (Merck, Germany), 25% ammonium hydroxide.

**Samples preparation** (2,10): The content of each syringe were dissolved directly in 2-8 mL methanol or Liquid-liquid extraction was performed as the content was dissolved in 1

mL of water and 0.1 mL of 5% of ammonium hydroxide was added to adjust the pH to 9.5. 2 mL of chloroform and 0.5mL isopropanol were added and the samples were processed on Vortex for 1 min. The resulting solution was filtered through a blue band, dried, dissolved in methanol and 1-2 μL of the organic phase were injected into the gas chromatograph.

**Equipment: GC/NPD:** Gas chromatograph with nitrogen-phosphorus detector GC / NPD (Thermo Finnigan), equipped with a capillary column Alltech EC-5 (30m L x 0.25 mm id), 0.25μm film 5% phenyl-95% dimethylpolysiloxane; temperature programming of the column: 200°C(2 min)/15°C/min/280°C, the temperatures of the detector and of the injector were 250°C, 1-2 μL sample in a methanol was injected in splitless mode of the flow. Duration of analysis - 15 min.

The identification was carried out according to the retention times of the analyzed components, compared with those of standard reference materials.

Under the described gas chromatographic conditions, the retention times of the analytes are: morphine - 6.40 min; codeine - 9.20 min; 6-MAM 10.33 min; diazepam - 9.05 min; papaverine - 13.33 min.

**GC-MS:** Gas chromatograph Thermo scientific, quadrupole mass spectrometry detector equipped; ionization mode with 70eV electron impact for ionization; capillary column InertCap 5MS/Sil ProG 2M 0.25mm x 30m id 0.25μm (Tokyo, Japan), temperature program 100°C (4 min)/15°C/min/290ºC. The temperature of the Injector was 250°C. The temperature of the detector was 290ºC. Carrier gas Helium with a flow 0.8 ml/min. Samples 1-2 μL volume in the methanol was injected in splitless mode; duration of analysis was 32 min; SCAN MODE: tracking mass units was conducted in the range from m/z 50 to m/z 400.

Under the described conditions, the retention times were as follows: nicotine - 9.25 min; pyracetam - 11.36 min; meconine - 12.73 min; hydrocotamine - 13.20 min; caffeine - 13.50 min; acetaminophen - 13.20 min; paracetamol - 16.20 min; codeine - 17.20 min; diazepam - 17.51 min; morphine - 17.74 min; acetyl codeine -17.91 min; 6-MAM 18.13 min; heroin -18.85 min; papaverine - 20.90 min; noscapine (narcotine) - 26.52 min. The identification was carried out using libraries of Wiley Registry of Mass Spectral Data 6 (2010), PMW-Tox 2, NIST for GC/MS.

## III. RESULTS

**Table 1** presents the results of forensic-chemical expertise to establish the composition (drugs and medicines) of 44 evidence - 41 syringes and three sachets of heroin powder using GC/NPD method. Figures 3a and 3b presented chromatograms of “dose” heroin power and in Figures 4a and 4b - chromatograms of heroin from syringes, obtained using GC/NPD method.

Acetylmorphine (heroin) prevails in the samples of heroin powder. 6-MAM (RT = 10.30 minutes) predominates in the majority of syringes of "cooked" heroin. This is an indicator of metabolized heroin because of "cooking". The content of heroin has decreased (RT = 11.30 min) in syringes, while 6-MAM has appears.

Table 1. Drugs and medicines identified in syringes and street heroin powder

| № | Object | Forensic chemical expertise ID | Identified drugs and medicines (GC/NPD method) |
|---|---|---|---|
| 1 | syringe | 129/1999 | heroin, 6-MAM, caffeine, diazepam |
| 2 | syringe | 230/1999 | heroin, 6-MAM, caffeine, diazepam |
| 3 | syringe | 259/1999 | heroin, 6-MAM, acetyl codeine, diazepam |
| 4 | syringe | 273/1999 | 6-MAM, acetyl codeine, morphine, papaverine |
| 5 | syringe | 26/2000 | morphine, caffeine, salicylate |
| 6 | syringe | 29/2000 | 6-MAM, morphine, caffeine, paracetamol |
| 7 | syringe | 36/2000 | heroin, 6-MAM, acetyl codeine, papaverine, diazepam |
| 8 | syringe | 54/2000 | heroin, 6-MAM, morphine, acetyl codeine, papaverine |
| 9 | syringe | 113/2000 | 6-MAM, bromazepam, diazepam |
| 10 | syringe | 118/2000 | 6-MAM, morphine, acetyl codeine, diazepam |
| 11 | syringe | 122/2000 | 6-MAM, morphine, acetyl codeine, diazepam |
| 12 | syringe | 180/2000 | heroin, 6-MAM , acetyl codeine, diazepam |
| 13 | syringe | 54/2001 | heroin, 6-MAM, papaverine, diazepam |
| 14 | syringe | 63_1/2001 | heroin, 6-MAM, papaverine, diazepam |
| 15 | syringe | 63_2/2001 | heroin, caffeine, diazepam, paracetamol |
| 16 | syringe | 63_3/2001 | heroin, caffeine, diazepam, paracetamol |
| 17 | syringe | 63_4/2001 | drugs and medicines have not been proven |
| 18 | syringe | 178/2001 | heroin, 6-MAM, morphine, acetyl codeine, diazepam, phenobarbitalum |
| 19 | syringe | 162/2002 | drugs and medicines have not been proven |
| 20 | syringe | 195/2004 | 6-MAM, morphine |
| 21 | syringe | 121_1/2005 | heroin, 6-MAM, |
| 22 | syrin | 121_2/20 | heroin, 6-MAM, |

| | | | |
|---|---|---|---|
| | ge | 05 | |
| 23 | syrin ge | 125_1/20 05 | heroin, 6-MAM, |
| 24 | syrin ge | 125_2/20 05 | drugs and medicines have not been proven |
| 25 | syrin ge | 358/2005 | heroin, caffeine, paracetamol |
| 26 | syrin ge | 370/2005 | heroin |
| 27 | syrin ge | 432/2005 | heroin |
| 28 | syrin ge | 12_1/200 6 | heroin, 6-MAM |
| 29 | syrin ge | 12_2/200 6 | heroin, 6-MAM |
| 30 | syrin ge | 72/2006 | heroin, 6-MAM |
| 31 | syrin ge | 128/2006 | heroin, 6-MAM |
| 32 | syrin ge | 180_1/20 06 | heroin, 6-MAM |
| 33 | syrin ge | 180_2/20 06 | heroin, 6-MAM, caffeine |
| 34 | syrin ge | 226_1/20 06 | heroin, 6-MAM, caffeine |
| 35 | syrin ge | 226_2/20 06 | heroin, 6-MAM |
| 36 | syrin ge | 351/2006 | heroin, 6-MAM, |
| 37 | syrin ge | 364/2006 | heroin, 6-MAM, acetyl codeine |
| 38 | syrin ge | 139/2007 | heroin, 6-MAM, |
| 39 | syrin ge | 65/2008 | heroin, 6-MAM, acetyl codeine, diazepam |
| 40 | syrin ge | 333/2011 | heroin, 6-MAM |
| 41 | syrin ge | 275/2012 | heroin 6-MAM, papaverine, noscapine (narcotine), acetyl codeine, caffeine |
| 42 | heroi n powd er | 180/2000 | heroin, 6-MAM, acetyl codeine, diazepam |
| 43 | heroi n powd er | 365/2006 | heroin, 6-MAM |
| 44 | heroi n powd er | 560/2010 | heroin, 6-MAM, caffeine |

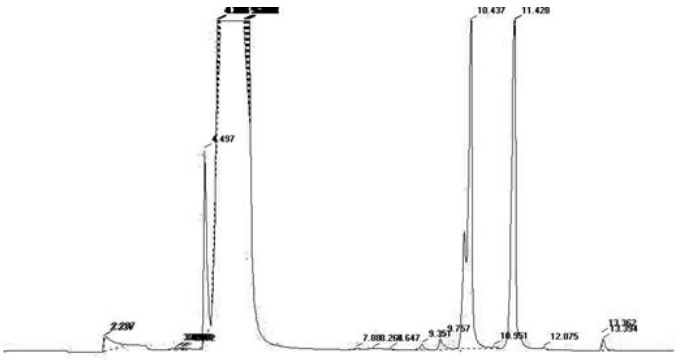


**Figure 3a. GC/NPD analysis of heroin powder (used on the street)**

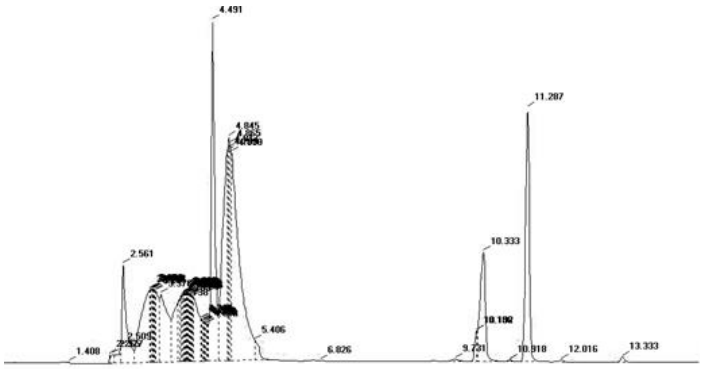


**Figure 3b. GC/NPD analysis of heroin powder (used on the street )**

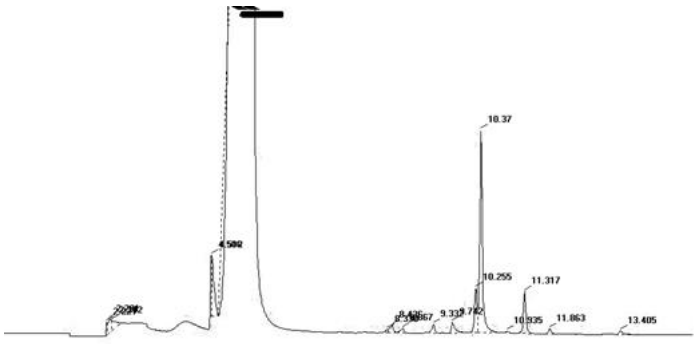


**Figure 4a. GC / NPD analysis of syringe of heroin used in the street**

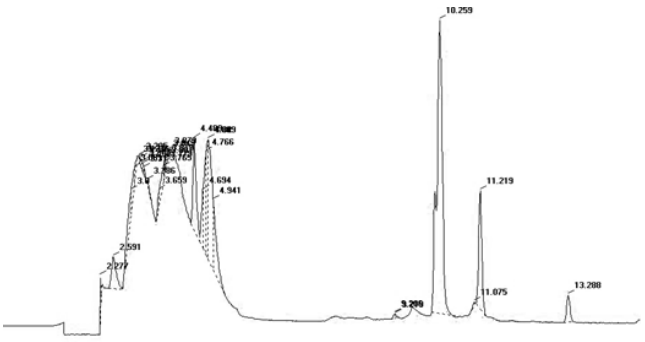


**Figure 4b. GC / NPD analysis of syringe of heroin used in the street**

Often in forensic chemical expertise is needed to conduct re-analysis after a long time. Meanwhile, material evidence are kept in the dark at room temperature. Because of the small amount of drug remaining in the evidence that was collected, analyzed objects are depleted after conduct of the analyzes for the identification. Duplicate study of stored objects (syringes, lids, spoons) have to be made about 10 years after the initial analysis to prove the drugs in them after the passage of time. For this purpose 17 available objects of material evidence (syringes, lids and spoons) were analyzed using a gas chromatograph with a Mass Selective Detector (GC-MS). All re-examined evidence materials had proven drugs with the exception of three syringes. Figure 5 presents the GC / MS chromatogram of a syringe used for application of heroin.

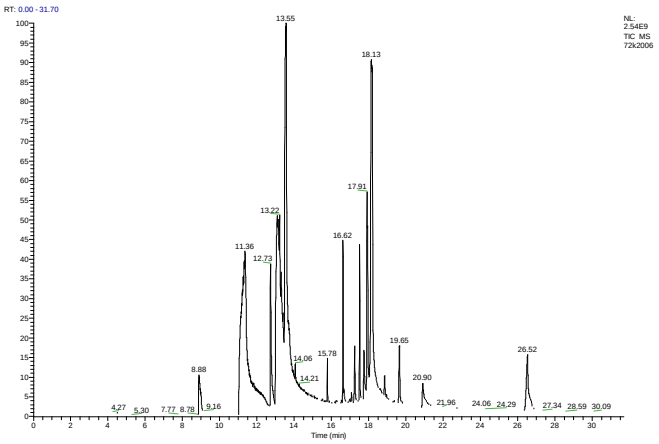


Figure 5. GC/MS analysis of evidence - syringe. Retention times in the order of appearance in chromatography: nicotine - 9,25 min; pyracetam - 11, 36 min; meconine - 12,73 min; , hydrocotamine - 13,20 min; caffeine - 13,50 min; acetyl amidofen - 13,20 min; paracetamol - 16,20 min; codeine - 7,20 min; diazepam - 17,51 min; morphine - 17,74 min; acetyl codeine - 17, 91 min; 6- MAM - 18,13 min; heroin - 18,85 min; papaverine - 20,90 min; noscapine (narcotine) - 26,52 min.

Table 2 presents the results of identified composition of drugs and medicines for 17 objects from Forensic chemical expertise after a storage period of about 10 years, using GC / MS.

Table 2. Establish the composition of drugs and medicines in the objects of Forensic chemical expertise after prolonged storage

| № | Object/ Forensic chemical expertise ID | Identified drugs and medicines (GC/MS method) |
|---|---|---|
| 1 | Cap Lab. ID 193/2005 | heroin, codeine, acetyl codeine, papaverine, noscapine (narcotine), paracetamol |
| 2 | Syringe Lab. ID 193/2005 | 6-MAM, caffeine, codeine, acetyl codeine, morphine, noscapine (narcotine), papaverine, diazepam, nordiazepam, benzophenone |
| 3 | Syringe Lab. ID 125/2005 | heroin, 6-MAM, codeine, acetyl codeine, paracetamol |
| 4 | Syringe Lab. ID 906/2005 | methadone |
| 5 | Syringe Lab. ID 811/2005 | drugs and medicines have not been proven |
| 6 | Syringe Lab. ID 36/ 2000 | drugs and medicines have not been proven |
| 7 | Syringe Lab. ID 105/2004 | drugs and medicines have not been proven |
| 8 | Syringe Lab. ID 358/2005 | caffeine, codeine, acetyl codeine, paracetamol |
| 9 | Syringe Lab. ID 52/2006 | 6-MAM, codeine, acetyl codeine, noscapine (narcotine), papaverine, paracetamol |
| 10 | Scoop Lab. ID 73/2006 | heroin, 6-MAM, caffeine, acetyl codeine, longifoliya, paracetamol |
| 11 | Cap 1 Lab. ID. 72/2006 | heroin, 6-MAM, caffeine, codeine, morphine, acetyl codeine, hydrocotamine, papaverine, noscapine (narcotine), meconine, pyracetam, glycerol; |
| 12 | Cap 2 Lab. ID 72/2006 | heroin, 6-MAM, caffeine, codeine, acetyl codeine, noscapine (narcotine), meconine, papaverine, pyracetam, paracetamol |
| 13 | Syringe Lab. ID 370/2005 | heroin, 6-MAM, caffeine, codeine, acetyl codeine, papaverine, noscapine (narcotine), meconine, pyracetam, paracetamol |

| | | |
|---|---|---|
| 14 | Cap Lab. ID 906/2005 | heroin, 6-MAM, caffeine, codeine, acetyl codeine, morphine, hydrocotamine, papaverine, noscapine (narcotine), meconine, nicotine |
| 15 | Scoop Lab. ID 2/2005 | heroin, 6-MAM, caffeine, codeine, morphine, noscapine (narcotine), meconine, longifulen, hydrocotamine, paracetamol, nicotine, papaverine |
| 16 | Scoop Lab. ID 3/2005 | heroin, 6-MAM, caffeine, acetyl codeine, noscapine (narcotine), papaverine, nicotine cocaine |
| 17 | Cap Lab. ID 3/ 2005 | drugs and medicines have not been proven |

## IV. DISCUSSION

In almost all the syringes (41 pieces) two main substances - heroin and its main metabolite 6-monoatsetilmorfin (6-MAM) have been identified as present in the samples. The main metabolite 6-MAM is prevalent in 80% of the syringes used for "cooked" heroin. In 46% of the syringes (19 pieces) were found also other opiate alkaloids. They originate from the production of heroin - acetylcodeine, morphine, caffeine, papaverine, noscapine (narcotine) and its metabolite mekonin. In a large number of syringes found at crime scenes, intentionally were added thinners (paracetamol amidofen, piracetam, salicylate) and psychoactive substances, mostly diazepam, but also nicotine and cocaine. In only one syringe was found intentionally added phenobarbital (syringe ID18). None of the syringes prove the presence of quinine and strychnine. In syringes collected as evidence before 2001, predominates the addition of the drug diazepam to heroin. After entering the special medical prescription of this drug in the pharmacy network in 2001, in later dated objects were detected other active substances - cocaine, methadone, nicotine, while diazepam was found more rarely.

## V. CONCLUSION

Qualitative analysis of the composition of the used drugs and medicines in the objects available and stored over 10 years of evidence (lids, syringes, spoons) was performed using GC/NPD and GC/MS. It was found that drug resistance allows the analysis of material evidence to be held even after a long period of time. Chromatographic conditions of GC-NPD and GC-MS methods used for identification of composition of drugs (heroin) and intentionally and non-intentionally added impurities in it, were described in detail and used in criminology. We have established differences in the composition of purposefully added drugs 10 years ago and recently.

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