POSSIBILITIES TO RECOGNIZE AND IDENTIFY - *HEROINE*

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Rezumat

În această lucrare sunt prezentate posibilităţile de recunoaştere şi de identificare a heroinei – substanţă cunoscută şi sub numele de „moarte albă". Recunoaşterea heroinei după caracteristicile generale are un caracter orientativ şi este menită să pună în gardă atât pe cei implicaţi în lupta antidrog, cât şi pe cei care vin în contact întâmplător, cu astfel de produse sau substanţe. Metodele de analiză prezentate sunt legate de proprietăţile fizice şi chimice ale heroinei şi oferă posibilitatea determinării calitative. Metoda de analiză prin cromatografie pe strat subţire (CSS) se pretează atât determinărilor calitative, cât şi determinărilor cantitative.

Abriss

Dieses Werk stellt die Erkennungs- und Identifizierungsmöglichkeiten der Heroin dar – Rauschgift erkannt als „der weiße Tod". Die Erkennung der Substanz ist Orientierungsmäßig für alle die in Verbindung mit dem Gift kommen sei es die in dem Antidrogekampf inbegriffen sind oder die was zufällig damit in Verbindung kommen. Die dargestellten Analysenmethoden bieten die Möglichkeit einer qualitativen Bestimmung dar. Die Dünnschichtchromatographie ist sehr geeignet für die qualitativen sowie auch quantitative Bestimmungen.

Résumé

Ce travail présente les possibilités de reconnaître et d'identifier l'héroïne – substance connue également sons le nom de "mort blanche". La reconnaissance de l'héroïne selon les caractéristiques générales a un aspect orienté et est destine de mettre en garde aussi les personnes impliquées dans la lutte antidrogue que celles qui en presentment accidentellement contact avec tells produits ou substances. Les méthodes d'analyse présentées sont liées aux propriétés physiques et chimiques d'héroïne et offrent la possibilité de la détermination qualitative. Les méthodes d'analyse á chromatographe sur concheminee (CSS) se prête également á des déterminations qualitatives.

Nowadays, drug addiction has become a strong "preoccupation" among the Romanian young people, especially teenagers. The Romanian society is totally unprepared to solve the serious problems represented by drug - dealing and drug - addiction. First a transit country, Romania became afterwards a consumer country, a country where the drug - dealing is more and more organized and where the number of clients - drug buyers and, implicitly, drug addicts - has grown a lot lately. Most of the persons who are addicted to psychoactive substances belong to a category of age of 19 - 20 years old. The persons addicted to drugs belong to all the school cycles: gymnasium, preuniversity and university level.

At present, all over the world, the consumption of psychoactive substances has become a serious and complex problem, involving a multitude of conflicts and needs. In the USA, drug consumption increased in the "90's", and the products on the drug market became more and more pure, still having the same price. If, in the "80's", the amount of heroine in a single dose was rather small, at present, it gets to 4 - 40 %, sometimes even to 60 - 70 %. [St 03]

On the Romanian drug market one can buy heroine at prices between 150000 - 200000 lei for a "little ball" (a dose of heroine having 0,02 g.). Heroine is much sought for because of its accessible price in comparison to other categories of drugs.

Heroine's General Characteristics

Heroine is a semisynthesis morphine derivative obtained by the acetylation of morphine and which behaves like a "prodrug" or a forerunner of morphine.

Heroine is the most powerful opium alkaloid, having the aspect of an extremely fine crystalline white powder. It has a bitter taste and it is soluble in water and alcohol. Heroine's bitter taste and its faint vinegar smell are due to the acetic anhydride. This product- absolutely indispensable for the manufacture of heroine- is a colourless liquid, with a pungent smell.

There are *4 types of heroine* on the illicit drug market, types that are codified with the following numbers: *1, 2, 3,* and *4*, having the same physical properties as the basis heroine.

- *Heroine number 1* – the drug, of **a beige – brown** colour, has a low heroine content and a large amount of heroine unconverted chemically.
- *Heroine number 2* - contains diacetylmorphine, in an intermediate stage of transformation, before being turned into chlorhydrate and before being supplemented with additives and diluters, which will create *Heroine number 3*. *Heroine number 2* is a solid product, which can be crushed between the fingers and turned into powder, and its colour varies from **grey to dark brown**. It is not soluble into water. *Heroine no. 1 and 2*, being less pure regarding the active substance contained, are no longer sought for by the heroine dealers and consumers. However, one would be totally wrong to consider these types of drugs as no longer present in the illicit drug - dealing circuit.
- *Heroine number 3* - is the drug, which generally has the shape of irregular granules, but it can also be found in the shape of powder. Its colour varies from **brown to dark grey**. Its main diluter is the caffeine, but sometimes, one can also add barbiturates, quinine, strychnine or scopolamine. Generally, heroine number 3 contains 25-45% diacetylmorphine, and the caffeine percent varies between 30-60%. It is known under various names: "Hong- Kong Rocks", "Brown Sugar", "Vogelfutter", etc.
- *Heroine number 4* - is injectable heroine. It has the aspect of a fine, **white or cream** - coloured powder, containing up to 98% diacetylmorphine chlorhydrate. Being submitted to a large level of purification while it is processed, it generally contains but few impurities. When sold by detail, it is diluted with lactose, caffeine or any other pharmacologically inert substance.

Lately, *Heroine no. 3 and 4* have shown up in the illicit trade with various colours: **brown, yellowish, pink or even red**, a fact that generally misleads those who come into contact with such substances. The deviation from heroine's usual colour is due either to the impurities that occur during manufacture or to the caution measures that the drug- dealers take in order to mislead the judiciary organs. For the very reason of misleading the authorities vigilance, the drug - dealers and the addicts mix up heroine with lactose, powdered sugar, condensed milk or other ingredients.

The external morphological examination (the first stage of laboratory examination) is done with the naked eye, in daylight or ultraviolet rays, taking note of the colour, the aspect and the smell.

It is to be mentioned that neither the colour, nor the smell have a certain individualization character, but they only offer information - sometimes precise enough - concerning the nature of the examined substance. This recognition has an orientative

character and it is meant to warn both those involved in the antidrug, fight and those who accidentally come into contact with such products or substances. [Be. 98], [Ţi 03]

Methods of Qualitative Analysis

Indexes, referring to the nature of the various substances discovered which arise suspicions concerning their belonging to the narcotics group result from the chemical and physico-chemical properties of each substance, when they are submitted to the identification analysis.

Chemical and physico-chemical methods are used in order to identify heroine and heroine chlorhydrate.

Chemical methods: - precipitation reactions;
- colour reactions.

1. Precipitation reactions:

• The reaction with **mercuric chloride in 5%** leads to the appearance of a precipitate, having the aspect of *dendrites*;

2. Colour reactions:

• By means of the reaction with **the Marquis reagent (formaldehyde in sulphuric acid)**, the result is a *cherry* colour;

• By means of the reaction with **the Frőhde reagent (sulphomolybdic acid)**, the result is a *red- purple-blue-green* colour;

• With **the Mandelin reagent, (ammonium sulphovanadate)**, the resulting colour is *blue-grey*;

• The **positive Vitali** reaction develops an *olive-green* colour;

• From a mixture of **nitric and phosphoric acid** results a *yellow up to brown red* colour, depending on the concentration;

• With the **cobalt thiocyanate**, the colour *turns purple*;

• Heroine chlorhydrate, in reaction with **the nitric acid**, develops a yellow- greenish colour;

• Heroine chlorhydrate yields a *dark green* colour, in reaction with **the potassium hexacyanoferrate (III) and ferric chloride in sulphuric acid**. [Pr 00]

Physico-chemical methods:
- microcrystalline analysis;
- solubility analysis;
- the melting point analysis;
- chromatography on thin layer (CSS);
- paper chromatography.

• In order to carry out heroine's *microcrystalline analysis*, the following steps are taken: we treat heroine with various reagents and we examine the types of crystals resulted. [Cl 86]
A series of reagents, as well as the shape of the crystals, are shown in table 1.

In order to determine heroine's solubility, we have to work according to the USP (United States Pharmacopea) stipulations. The solvent used is a mixture of hexane-dioxane in 3:1 ratio for heroine (solubility 13 mg/l). For heroine chlorhydrate, we can use only dioxane, (solubility 26 mg/l). The commercial solvents (hexane and dioxane) are distilled in a rotary vapour and they are degasified before blending. The bath temperature is 25°C and we can work at 28 rotations / minute. [Do 81]

Table 1

MICROCRYSTALLINE TESTS

Reagent	Type of crystal
Mercuric iodide	Needles
Sodium acetate	Hexagonal
Platinum chloride	Needles
Auric bromide	Needles
Mercuric chloride in hydrochloric acid	Plates and needles
Iodine in potassium iodide	Plates and needles
Bromide-auric acid-phosphoric acid-hydrobromic acid	Amorphous precipitate or irregular plates

• Heroine and heroine chlorhydrate's *solubility* at room temperature is presented in table 2:

Table 2

Heroine and heroine chlorhydrate's solubility at room temperature (g/l)

Solvent	Solubility (g/l)	
	Heroine	Heroine chlorhydrate
Water	1:1700	1:1,6 or 1:2
Ethanol	1:31	1:12 or 1:11
Ether	1:100	Insoluble
Chlorophorm	1:1,5	1:1,6
Alkali	Soluble	-

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• The value of *the melting point* of a substance represents one of the individual features with a sure identification value. But, exactly as in the case of the crystallographic determination, the melting point determination is also conditioned by the purity of the tested substance, any impurity causing value modifications. This is the reason why the respective test is particularly used in order to confirm the identity of a substance, established by means of other methods. The melting point of a heroine sample is at 170^{0}C, but some authors reported different values in the interval 170^0-174^{0}C. [Be 98], [Cl 86]

• *Chromatography on thin layer (CSS)* is frequently used for the qualitative analysis, but, under well-checked circumstances, it can also lead to drug quantification. For heroine's identification, the experimental conditions concerning the stationary phase, the mobile phase, the detection method and the retention factor are shown in table 3. [Do 81]

The meaning of the letters in column 3 is:

A – U.V. light with small wavelength;

B – U.V. light with medium wavelength;

C - Iodine 0,5% in chlorophorm;

D - potassium iodoplatinatum solution, followed by exposure to ammonium vapours;

E - sprinkling with potassium iodoplatinatum;

F - sprinkling with Dragendorff reagent, followed by heating at 120°C for 5 minutes and sprinkling with sulphuric acid;
G - sprinkling with potassium permanganate;
H - sprinkling with cobalt thyocyanate;
I - sprinkling wityh bromine cresol green;
J - sprinkling with iodine solution in methanol and copper chloride;
K - sprinkling with diluted hydrochloric acid;

The analysis through chromatography on thin layer (CSS) can also be applied in the analysis of the opiates in urine: heroine, 6-monoacetylmorphine, morphine and codeine. An amount of 5 ml of urine form a heroine addict or a poppy seeds addict and 5 ml of control solution (morphine and codeine 200 ng/ml) is acidulated with 500 µl of acetic acid 1M. The solutions resulted are centrifuged for 5 minutes. The mixture is purified by means of extraction in solid stage on a SPEC – LTD.- MP3 column, with an aspiration of 60 kPa (2 ml/min), storing the drugs on the absorbent layer in the reagent tank from the bottom of the column. The drugs are eluted with ethyl acetate/concentrated ammonium (49:1) in inoculation disks. The disks are moved along some control disks, each of them containing opiate partially impregnated on plates with silicic acid, pretreated with metavanadate salts. The mobile phase is formed of 3 ml dichlormethane - methanol (19:1), containing 30 µl concentrated ammonium. After drying, the plates are submerged in sulphuric acid, in order to notice the colour of the spots. The detection limits are included in the interval: 100 – 130 ng/ml. The presence of the heroine's metabolite, the monoacetylmorphine, can be noticed only in the heroine addicts' urine, so this method can be used in order to identify it. [Bo 98]

Table 3

HEROINE'S ANALYSIS THROUGH (CSS)

Stationary phase	Mobile phase	Detection methods	R_f x 100
silica gel	methanol : ammonium (100 : 1,5)	A, B, C, D, E, J	45, 38, 50
silica gel	ammonium : benzene : dioxane : ethanol (5 : 50 : 40 : 5)	B	76, 60
silica gel	acetic acid : ethanol : water (30 : 60 :10)	A, B, C, D	35, 44, 50, 35, 35
silica gel F254	benzene : dioxane : ethanol : ammonium (10 : 8 : 1 : 1)	A, B, C, D	46, 76
silica gel F254	methanol	A, B, C, D	38
cellulose	2-propanol : water : icy acetic acid (8 : 1:1)	A, B, C, D	72
silica gel	Butylic ether : ethylic ether : diethylamine (45 : 45 : 10)	A	44
silica gel	chlorophorm : dioxane : ethyl acetate : ammonium (25 : 60 : 10 : 50)	A	85
silica gel	chlorophorm : methanol (9:1)	A, C, J	61

The simultaneous detection of heroine's impurities and coextractors can be carrieed out by means of CSS with 2 successive mobile phases. Thus, the methanolyc solutions (standards of 1-2 ml, samples of 2-3 mg/ l) are analysed on silica gel plates 60 F254 (10 cm x 10cm x 0,25 mm - the thickness of the layer), with the mobile phase formed of benzene/

acetonitryl/ methanol (8 : 1 : 1). After drying, the plates are submerged for elution in the same direction in a ferry, containing cyclohexane/ toluene/ diethylamine (15 : 3 : 1,8). The detection is realized in U.V. light, at the wavelength of 254 nm. [Kr 97]

Another method of identifying heroine by means of CSS uses portions of 10 µl of heroine solution, applied on silicagel plates and eluted with chlorophorm-ethanol (9 :1). After drying, the plates are sprinkled with mercury chloride 1% - potassium ferricyanide (1:1) and dried at 80°C, in the drying stove for 5 minutes. The appearance of some dark blue spots indicates the presence of some quantities of heroine larger or equal to 1 µg (R_f = 0,54). Metaqualone, benzodiazepines, phenobarbitone and caffeine don't yield spots. Opiates and procaine yield blue spots having different R_f. The blue complex has its maximum of absorbance at 580 nm and it is stable at pH = 2,62. [Ka 97]

The heroine samples are applied on F254 silica gel plates and are eluted with a mixture of chlorophorm and ethanol (9:1). After drying, the plates at 100°C for 5 minutes, they are sprinkled with a mixture of copper chloride 1% – potassium ferrocyanide 1% (1:1), yielding dark brown spots. Other opiates yield similar spots, but with different R_f values. The detection limit is 1 µg of heroine. [Ka 96]

Amounts of 10 µl ethanolic solutions of heroine, cocaine and codeine are separated by CSS on cellulose plates (0,1 mm). The mobile phase is formed of ethyl acetate/ methanol/ ammonium in 25% (2:9:9). The individual spots are drawn from the plate and are analysed by means of spectrophotometry in I.R. with a Fourier transformer. The spectres are registered on a BioRad-Digilab 60A instrument, equiped with an Interferometer 896 and a detector DTGS. In order to eliminate the cellulose matrix, the spectral subtraction is performed. The calibration diagrams are linear in the 2-10 µg domain. The detection limit is 2 µg. [Mi 95]

• For heroine's qualitative determination by means of *chromatography on paper*, one can use the upward method with a normal or inverted phase. The visualization of the resulting spots can be done in UV light or by sprinkling them with various reagents. For example, the chromatographic analysis on upward paper can be realized using Whatman 1 blotter paper by submerging it in monosodic citrate 5% solution, then drying it at 25°C for an hour, with the mobile phase formed of a mixture of 4,8 g of citric acid in 130 ml water and 870 ml 1-butanol. The sample is formed of a heroine solution 1% in acetic acid 2N, hydrochloric acid 2N, sodium hydroxide 2N or ethanol. The visualization of the resulting spots is realized in U.V. or by sprinkling them with a solution of potassium iodoplatinatum.

The value of the retention factor is R_f =0,33.

Another method of chromatography on upward paper with an inverted phase is realized on Whatman 1 or 3 paper, impregnated with a solution of tributirin 10% in acetone and drying it in the open air. A blotter solution of acetate (pH= 4,58) is used as a mobile phase. The samples analysed can be ethanolic or chlorophormic solutions with a concentration of 1 - 5%. Potassium iodoplatinatum is used as a localization reagent. The R_f value is 0,84.

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An alternative of this method uses as a mobile phase a solution of blotter phosphate (pH = 7,4), a case when the R_f value is 0,12. Other methods of heroine identification through chromatography on paper can also be used, as it is shown on table 4. [Do 81]

Table 4

HEROINE'S ANALYSIS THROUGH CHROMATOGRAPHY ON PAPER

Paper + treatment	Mobile phase	Detection	R_f x 100
Whatman 1 + formaldehyde + acetic acid 1%	chlorophorm	-	76
Whatman 1 + zirconium phosphate	acetic acid 5%	-	33
Whatman 1	1-butanol : icy acetic acid : water (12: 3:5)	C, E, G, H, I	74
Whatman 1	1-butanol : sodium acetate 1N : HCl 1N (7: 120: 60)	C, E, G, H, I	89
Whartman 1 impregnated with monosodic citrate 5%	1-butanol : sodium acetate 1N : water (12: 3:5)	C, E, G, H, I	32
Whatman 1 impregnated with monosodic citrate 5%	1-butanol : sodium acetate 1N: HCl 1N (7: 120: 60)	C, E, G, H, I	16

Conclusions

Lately, an extraordinary recrudescence of the drug scourge can be noticed. The drugs contaminate, corrupt, morally destroy individuals and societies, breaking off innocent lives. That's why the responsible factors must be compelled to adopt urgent measures in order to stop this dreadful race towards nothingness.

The impact of heroine addiction - a substance also known as the "white death" - is devastating. Young people and especially children's heroinomania should cause particular anxiety.

This paper deals with the possibilities to recognize and identify heroine. The first step in the identification of heroine or of any other drug is, as mentioned before, the recognition of its general features, these depending on its external morphologic aspect.

The colour reactions - and, to a small extent, the precipitation reactions -, even though they can't replace lab analyses, are those who assure a first approach of a sample composition that would contain heroine.

The most frequently used methods in the specialized analysis laboratories are: chromatography on paper and chromatography on thin layer (CSS). These methods have a series of advantages:

- the apparatus used are simple and the cost price is low;
- the possibility of working simultaneously on more samples, including - witness samples;
- a great flexibility in choosing the stationary and mobile phase;
- a small amount of spotted solution;
- rapidity in realizing the determinations without being necessary the employment of apparatus;

These methods are separation techniques under well - controlled circumstances that lead both to heroine's identification and to its quantification. They are continually improved, considerable progress being registered in the field of the solvent systems and the visualization of the components on chromatographic plates.

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