

COMPLEX HEROIN COMPARISON INVESTIGATION

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ABSTRACT: The identification and quantitation of illicit heroin samples are not more the problem for the forensic laboratories. The main problem is the defining the origin and the similarity of the heroin samples. The complex method of heroin investigation is proposed. Method based on the following stages: 1. identification and 2. quantitation of major constituents of heroin: opium alkaloids and its derivatives, other drugs (cocaine etc.) and adulterants (aspirin, diphenhydriate, caffeine etc.) by chromatografic methods, 3. characterisation of trace level impurities (neutral and acidic products) – impurity profiling by GC/MS, 4. identification of diluents (sugars, starch, soda) by IR spectroscopy. The criteria of similarity based on whole complex method were defined. For every analytical technique presented parameters are adduced.

KEY WORDS: Heroin; Chromatography; Impurity profiling.

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INTRODUCTION

During last several years the drug illicit market in Russia had considerable changed. Up the middle of 90th the main narcotic drugs were plant drugs – marihuana, poppy straw, opium, but now days – heroin is the main drug. It substitutes the plant and most synthetic drugs at illicit market in Russia. The main regions of manufacturing of “Russian” heroin are the republics of the Middle Asia, Afghanistan and Pakistan. And for the solving the problems of the determining the origin of seized heroin samples our laboratory began to use heroin comparison method.

EXPERIMENTAL

Apparatus

Gas chromatograph: Hewlett-Packard 5890 series II plus, equipped with flame ionization detector was used. The capillary column used was a fused silica, HP-5 25 m × 0.20 mm with 0.33 micron film thickness. Carrier gas was nitrogen with an average gas velocity of 12 cm/s.

Gas chromatograph-mass-spectrometer: Hewlett-Packard 5890 series II plus and 5972 mass selective quadrupole detector. The capillary column used was a fused silica, HP-5 25 m x 0.20 mm with 0.33 micron film thickness. Carrier gas was helium with an average gas velocity of 30 cm/s.

HPLC chromatograph: Milichrom series 4 ("Medikant", Russia), equipped with programmed UV-detector. Column: Separon SGS C-18, 80 x 2 mm, 5 micron particles. Mobile phase: phosphate buffer-acetonitrile with diethylamine, pH 3.0; flow velocity – 120 mkl/min; detection at 210, 220, 230, 250 and 280 nm, simultaneously.

IR spectrometer: IR microscope model "IR-Plan" Spectratech (USA), coupled with IR-Furie spectrometer Perkin Elmer in wave length range 4000–650 cm^{-1} , resolution 4 cm^{-1} , scan numbers – 132, upper masking aperture, detector MCT-B, objective – Reflashromat-15X.

Quantitation analysis of heroin samples: the oven temperature program used started with initial temperature of 200°C with 1 min hold, then ramped at 15°C/min to 280°C followed by final hold of 7 min. Detector temperature was held at 290°C. Quantitation is made by internal standard method.

Impurity profiling analysis: the oven temperature program used started with initial temperature of 50°C with 1 min hold, then ramped at 15°C/min to 310°C followed by final hold of 20 min. Temperature of interface of mass selective detector was held at 310°C. The injection volume – 2 mkl, splitless injection. Electron impact mass spectra were collected at an ionisation potential of 70 eV.

Internal standard solutions

The internal standard solution for GC quantitative analysis of heroin samples was prepared by making 1.0 mg/ml solution of docosane in chloroform.

For HPLC the absolute calibration method was used.

Sample preparation for impurity profiling

From illicit heroin sample [1, 3] an amount equivalent to 15 mg diacetylmorphine is weighted in glass tube, dissolved in 5 ml 0.5 M sulphuric acid. The solution is extracted for three times by 5 ml toluene in ultrasonic bath for 10 minutes, extracts combined, the organic layer (3 ml) is transferred to glass tube and solvent is evaporated. The residue is dissolved in 100 mkl of toluene and analysed by GC/MS.

RESULTS AND DISCUSSIONS

This investigation based on the method, used by drug labs of the ENFSI-members [2, 4], modified and adopted. The complex method is fulfilling in 5 stages.

At the first stage after visual examination, the verifying on solubility in several solvents (water, ester, chloroform) is made. The conclusions of the solubility of the illicit heroin sample will be useful for future investigation by GC and HPLC.

At the second stage the qualitative analysis of sample is made. For this purpose GC/MS is usually used. A part of sample is dissolved in methanol or in water, then 2–3 drops of ammonia added, extracted with chloroform (pentane) and organic extract is analysed by GC/MS. In some cases for identification of components HPLC technique can be helpful.

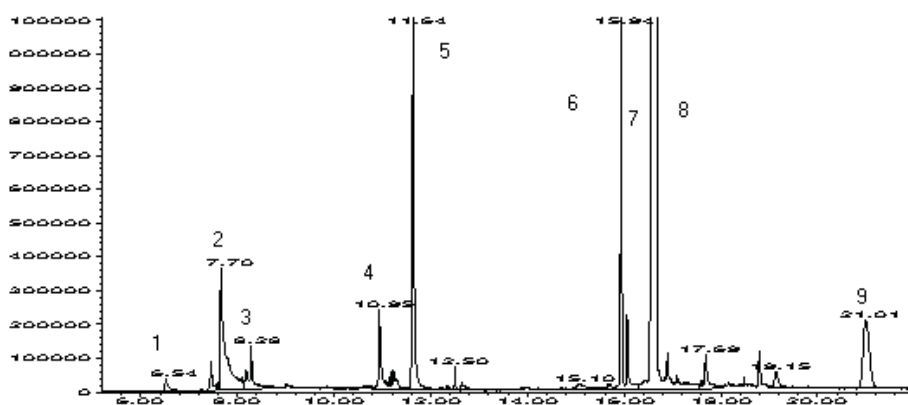


Fig. 1. Total ion chromatogram of methanol extract of illicit heroin sample. 1 – methylsalicylate, 2 – pelargon, 3 – salicylic acid, 4 – meconine 5 – caffeine, 6 – acetylcodeine, 7 – monoacetylmorphine, 8 – heroin, 9 – papaverine.

At the third stage the quantitative analysis of diacetylmorphine, 0⁶-monoacetylmorphine and acetylcodeine, opium alkaloids (morphine, codeine, papaverine, narcotine) is made. If some other drugs (e.g. cocaine) or adulterants (caffeine, acetaminophen, aspirin, diphenhydrinate, ascorbic acid, phenobarbital) are present in seized sample then their contents are also determined. Quantitative determination is made by GC and HPLC.

At the fourth stage – determination by IR spectroscopy of diluents such as sugars (glucose, lactose, fructose, maltose), starch, soda, flour. In one region the ferment lidase was used as a diluent.

At the last stage – impurity profiling. Comparison of chromatogram is based, at first, on chemical identification of all significant peaks (more than 10% of the largest peak) by GC/MS, using mass-spectral libraries (Wiley 278, NIST 98), Kovatch retention indexes and then after normalisation peaks by height – relative contents the defined peaks.

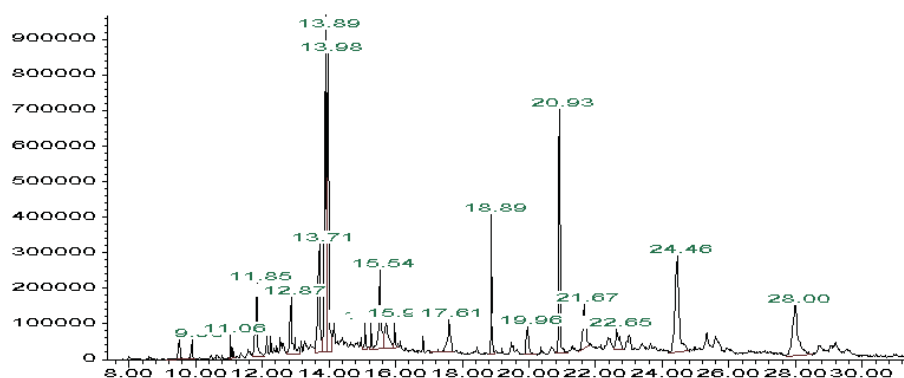


Fig. 2. Total ion chromatogram of toluene extract of illicit heroin sample – impurity profiling.

CONCLUSIONS

This complex method of heroin comparison requires about 50–100 mg of seized sample. The conclusions on similarity of heroin samples are following:

- if quantitative contents of diacetylmorphine, 0⁶-monoacetylmorphine, acetylcodeine, opium alkaloids and adulterants are equal, diluents are the same and the impurity profile are similar then it can be concluded that the investigated samples can have the same origin;
- if quantitative contents of diacetylmorphine, 0⁶-monoacetylmorphine, acetylcodeine, opium alkaloids and adulterants are not equal, diluents are different, but the impurity profile are similar then it can be concluded that the diacetylmorphine in investigated samples can have the same origin;
- if quantitative contents of diacetylmorphine, 0⁶-monoacetylmorphine, acetylcodeine, opium alkaloids and adulterants are not equal, diluents, and the impurity profile are different then it can be concluded that the samples are also different.

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