NACIONALNI FORENZIČNI LABORATORIJ
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EUROPEAN PROJECT RESPONSE to challenges in forensic drugs analyses

QUALITATIVE DETERMINATION OF RESIDUAL SOLVENTS IN COCAINE SAMPLES BY STATIC HEADSPACE-GC-MS (DEVELOPMENT OF COCAINE PROFILING METHODOLOGY)

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INTRODUCTION

A method for the determination of volatile compounds, utilized in illicit cocaine production, was developed. Static headspace analyses were performed on a GC-MS Model 7890-5975C (Agilent Technologies), equipped with a MPS 2 robotic sampler with a heated headspace syringe (Gerstel). The critical instrumental parameters were optimized as well their effects evaluated.

Samples of cocaine (hydrochloride) were obtained from 53 "unlinked" and 7 "linked" seizures by the Slovenian Police in the period from October 2014 to February 2016. Over 60 different volatile compounds were detected. Most of them were identified as residuals solvents, occluded in the crystal matrix of the final cocaine product. The rest of identified compounds were most likely by products-artifacts, formed during the processing of illicit cocaine (methyl benzoat, chloromethan, chloroethan, etc.) and other impurities (e.g. fatty acid esters).

Additionally, the method has been establishing for estimating if cocaine samples are linked or not. Validation parameters of method such as repeatability, precision, robustness and limits of detection limits for target compounds were determined.

EXPERIMENTAL PART

Preparation of cocaine samples for Headspace-Gas Chromatography-Mass Spectrometry

Homogenized sample was accurately weighted (an aliquot equivalent to 100 mg of pure cocaine) into 20-ml HS vial. A 10.0 ml portion of ultra pure water (<0,1 µS) saturated with 22% sodium sulphate is added followed by crimp capping.

Headspace extraction

The samples were incubated at 80°C for 40 minutes. One millilitre of sample headspace was introduced into the GC Inlet.

Gas Chromatography-Mass Spectrometry

GC was equipped with an Agilent J&W DB-624 UI capillary column (length 30 m, I.D. 0.32 mm, film thickness 1.8 µm). Helium was the carrier gas (constant flow was 2.2 ml/min), the injector port was maintained at 140 °C in split mode with a split ratio of 10:1. Column oven was temperature programmed as follows: initial temperature of 35 °C, initial hold 16 min, temperature program rates, 10°C/min to 100 °C, 5°C/min to 120 °C, 15°C/min to 160 °C, and 30°C/min to 240 °C, final hold 3.8 min. Total chromatogram run time was 35.6 min. The mass spectrometer was operated at 230 °C in scan mode with range of 40-200 amu.

HS-GC-MS RESULTS

Figures 1, 2 and 3 present a typical cocaine sample chromatograms containing a different types of most abounded residual solvents peaks. Results of identified compounds, frequency of appearances, limits of detection of compounds (targets ions) are summarized in Table 1.

Table 1: Summary of analytical results of occluded volatile compounds in cocaine samples.

Peak no.	Compound name	Possible origin(s) of compound	Frequency of apperance (%) of the target peaks	Target ion (m/z)*	Limit of detection of target ion (ug)	Integration: target ion + Q ion-s (m/z)*
1	CH3Cl	by-product in cocaine production	100,00	50,00	not defined	50+52+49
2	methyl ethyl ether	unknown source (most likely by-product)	96,10	45,00	not defined	45+60+59
3	CH3CH2Cl	by-product in cocaine production	92,20	64,00	not defined	64+66+49
4	methyl *i* -propyl	component in oxygenate solvent	9,80	74,00	not defined	74+59+43
5	ethanol	solvent or by-product in cocaine production	96,10	46,00	0,79	46+45+43
6	diethyl ether	oxygenate solvent	45,10	74,00	0,36	74+59+45
7	*2* -chloropropane	by-product in cocaine production	9,80	78,00	not defined	78+63+43
8	methyl propyl ether	solvent (used as an alternative to diethyl ether)	33,30	74,00	0,71	74+45
9	acetone	oxygenated solvent	51,00	58,00	not defined	58+42
10	Isopropanol	oxygenated solvent	49,00	59,00	7,85	59+45+43
11	methyl acetate	by-product in cocaine production	84,30	74,00	0,93	74+43+59
12	CH2Cl2	solvent	60,80	84,00	0,07	84+49+86
13	methyl pentan	petroluem ether	78,40	57,00	not defined	57+56+41
14	*i*- butyl methyl eter	component in oxygenated solvent	11,80	88,00	not defined	88+45+56
15	hexane	petroluem ether	80,40	57,00	0,07	45+41+43+56
16	*n* -propanol	oxygenated solvent	35,30	59,00	16,00	59+42+60
17	*2* -butanone (MEK)	oxygenated solvent	51,00	72,00	0,81	72+43+57
18	ethyl acetate	oxygenated solvent	92,20	88,00	4,50	88+70
19	CHCl3	solvent	13,70	83,00	0,07	83, 84, 47, 87
20	methyl hexane	petroluem ether	76,50	70,00	not defined	70+71+43+57
21	benzene	solvent	94,10	78,00	0,04	78-77
22	*i*- propyl acetate	component in solvent (thinner)	68,60	87,00	0,87	87+43+61+59
23	heptan	petroluem ether	76,50	71,00	not defined	71+43+41+57
24	Me-cyclohexane	petroluem ether	76,50	83,00	not defined	83+55+41+98
25	*n* -propyl acetate	thinner, oxygenated solvent	80,40	73,00	0,45	73+43+61
26	toluene	solvent, thinner, gasoline, petroleum distillate	100,00	65,00	0,22	65+91+92
27	*i*- butyl acetate	thinner, solvent	72,50	73,00	not defined	73+43
28	mesityl oxide	component in oxy. solvent (e.g. acetone)	33,30	98,00	0,43	98+83+55+43
29	butyl acetate	component in oxygenated solvent	23,50	73,00	not defined	73+43+56+61
30	*i*- propyl butanoate	component in oxygenated solvent	7,80	102,00	not defined	102+57+41+85
31	ethyl isovalerate	unknown origin (solvent impurity)	5,80	88,00	0,09	88+57+85+60
32	ethylbenzene	solvent, thinner, gasoline, petroleum distillate	100,00	106,00	not defined	106+91+65+77
33	p/m-xylenes	solvent, thinner, gasoline, petroleum distillate	100,00	105,00	0,04	105+106+91
34	propyl butanoate	component in oxygenated solvent	2,00	101,00	0,44	101+71+43+89
35	methyl palmitate	coca plant or production impurites	17,60	101,00	not defined	101+74+87+43
36	decane	often detected	43,10	85,00	often detected	85+57+43+142
37	ethyl palmitate	coca plant or production impurites	88,20	99,00	not defined	99+88+60+61
38	trimethylbenzene	the most abundand C3-alkyl benzen	100,00	120,00	not defined	120+105
39	*i* -propyl palmitate	coca plant or production impurites	27,50	99,00	not defined	99+60+71+117
40	propyl palmitate	coca plant or production impurites	41,20	99,00	not defined	99+117+61+60
41	methyl benzoate	from cocaine decomposition	92,20	136,00	0,11	136+105+77+51
42	butyl palmitate	coca plant or production impurites	39,20	99,00	not defined	99+56+71+117
43	ethyl benzoate	production impurites	80,40	150,00	0,05	150+105+77+122

*** Target and Q-ions are chosen based on mitigation of possible coelution interferences. Integration signals for acetone, ethyl acetate and toluene were deliberately attenuated by selected less abounded ions.**

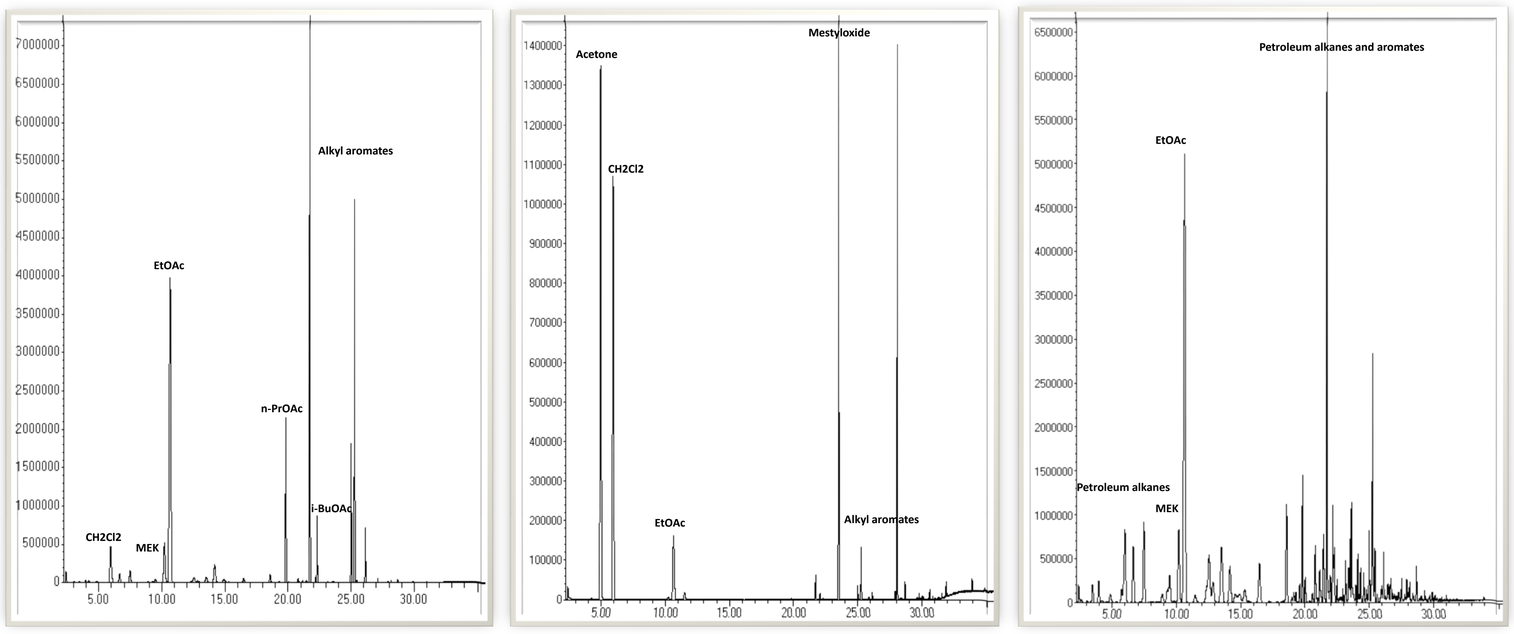

Fig. 1-3: Typical TIC chromatograms of the cocaine samples, containing traces of occluded oxygenated /halogenated solvents and petroleum hidrocarbons (e.g. gasoline and petroleum distillate).

DEVELOPMENT OF COCAINE PROFILING METHOD

Approx. 43 volatile compounds were preliminary established as variables for profiling methodology. The areas of all compounds were determined by the integrations of selected ions (see Table 1). Figure 4 shows the descriptive statistics of each compound in the form of box plot. The repeatability (analysis of the same sample, repeated six times, and analysis of the linked samples from same batch) and the precision of the method over few months (analysis of control sample) were determined by the variation of the pair wise Person correlation coefficient values. The influence of cutting agents on profile was carried out. For all additives, except lidocaine over 50% dilution, influence was not observed. In comparison between results of linked and non-linked samples, Pearson allows a very good "profiling" discrimination. The final selection of thresholds of decision for batch linkage has not yet been determined.

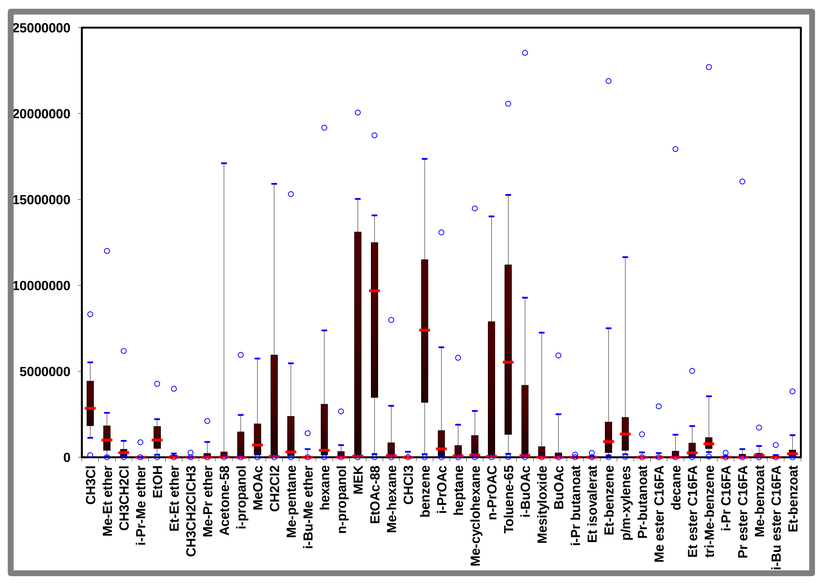

Fig. 4: Box plot representation of the 43 potentional variables.

CONCLUSION

- **HS-GC-MS and data analysis methods were developed for detection, identification as well as determination of volatile compounds profile.**
- **Validation of the most relevant method parameters were performed and evaluated. The detection limits of typical compounds from chemically different groups are between 0,04 µg - 16,00 µg. The chromatographic profile of cocaine sample was not influenced by time (reproducibilty) and additives (except lidocaine over 50% dilution).**
- **In every cocaine samples, analysis confirmed the presence of hydrocarbons, consistent with the use of gasoline and/or petroleum distillate (e.g. kerosene) during extraction of cocaine from coca leaf.**
- **Ethyl acetate (92%), *n*-propyl acetate (80%), *i*-butyl acetate (73%), acetone (61%), diethyl ether (45%), etc., are the most frequently encountered oxygenate solvents, used in cocaine hydrochloride preparation.**
- **Method shows high potential for cocaine batch comparison. The further optimization of "profiling" is in progress.**

Co-funded by the Prevention of and Fight against Crime Programme of the European Union

This work has been produced with the financial support of the Prevention of and fight against crime Programme of the European Union (grant agreement number JUST/2013/ISEC/DRUGS/AG/6413). The contents of this publication are the sole responsibility of the authors and can in no way be taken to reflect the views of the European Commission.

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