Unusual ways of cocaine smuggling

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1. Introduction

Analytical findings of four interesting cocaine case studies are presented. We applied GC-MS, SEM-EDX in some cases, FTIR analyses and different presumptive tests as well. Results are shown below.

2. Results

Case 1: COCAINE - POLYSTYRENE SOLID SOLUTION

In the year 2007 the statue of mother with child was seized at the Airport Ljubljana, Slovenia. Neto weight of the statue was 2106 g. The statue was composed of two layers: an inner layer and an outer protective layer. From the backside of the statue five holes were drilled to get representative samples for the analysis. The samples were presumptive tested and analysed by Agilent 6890-5975 GC-MS. The obtained analytical results are shown below:

Presumptive tests		Results
1.	Test on cocaine with cobalt thiocyanate reagent	(?) uncertain result
2.	Test on alkaloids with Bertrand's reagent	positive
3.	Test on halogenide ions with silver nitrate solution	negative

Qualitative analysis

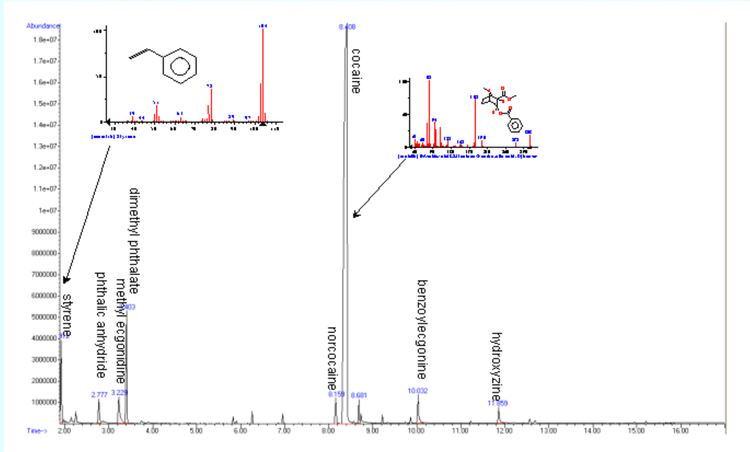
Retention time (min)	Compound	Retention time (min)	Compound
1,9	styrene	8,2	norcocaine
2,8	phthalic anhydride	8,4	*cocaine*
3,2	methyl ecgonidine	10,0	benzoylecgonine
3,4	dimethyl phthalate	11,9	hydroxyzine

In the protective layer only styren and dimethyl phthalate were identified.

Quantitative analysis

Cocaine concentration was 24 % (expressed as base form), what is equivalent to 460 g cocaine in statue.

Qualitative analysis by GC-MS (Agilent 6890N-5975B)



TIC OF SAMPLE

Case 2: COCAINE IN 2-BUTOXYETHANOL

In the year 2008, a mixture of solution and solid precipitate was discovered in the hydraulic press during custom examination of a cargo ship at the Port of Koper. The weight of confiscated suspicious material was 382 kg. The samples were Presumptive tested and analysed by GC-MS as well. Analytical results are shown below:

Presumptive tests		Results
1.	Test on cocaine with cobalt thiocyanate reagent	negative
2.	Test on alkaloids with Bertrand's reagent	positive
3.	Test on halogenide ions with silver nitrate solution	positive

Qualitative analysis

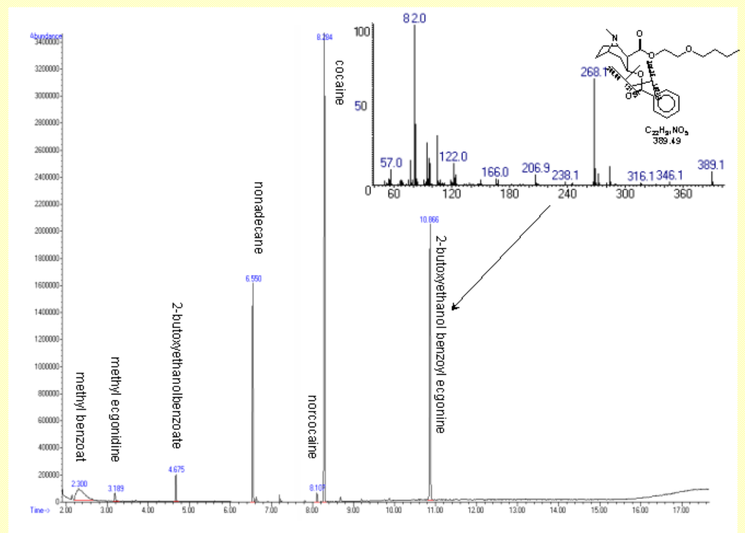
Retention time (min)	Compound	Retention time (min)	Compound
2,1	methyl benzoat	8,1	norcocaine
3,2	methyl ecgonidine	8,3	cocaine
4,7	2-butoxyethanolbenzoate	10,9	2-butoxyethanol benzoyl ecgonine
6,6	nonadecane (internal standard)	/	/

Under modified GC conditions (the starting oven temperature was 45°C) 2-butoxyethanol was detected as well. We supposed that 2-butoxyethanol benzoyl ecgonine was formed by transesterification reaction between 2-butoxyethanol (solvent in which cocaine was dissolved) and cocaine. GC-MS analysis of derivatized sample revealed the presence of fatty acids (palmitic acid, oleinic acid, linolenic acid, stearic acid).

Quantitative analysis

Concentration of cocaine in the solution was 3,7%, and in the precipitate 7,2 %. In the whole sample 16,9 kg of pure cocaine was calculated.

Qualitative analysis by GC-MS (Agilent 6890N-5975B)



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Case 3: COTTON SWABS IMPREGNATED WITH COCAINE

A DHL package shipped from Argentina was seized at the national airport Ljubljana in the year 2009. The package was a kind of handmade "cookbook" where two by two sheets of paper were laminated together. Between them we found ten hidden cotton swabs impregnated with an unknown substance. The total mass of isolated unknown substance was 464 g. Analyses revealed that the swabs were impregnated by cocaine. Presumptive test and GC-MS results are shown below:

Presumptive tests		Results
1.	Test on cocaine with cobalt thiocyanate solution	positive reaction
2.	Test on chloride with silver nitrate solution	positive reaction

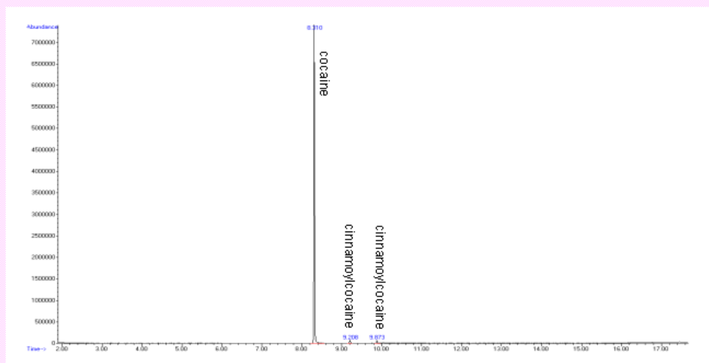
Qualitative GC- MS analysis (extraction in $CHCl_3$)

Retention time (min)	Compound	Retention time (min)	Compound
8,3	cocaine	9,2; 9,8	cinnamoylcocaine

Quantitative analysis

The concentration of cocaine in the sample was 87,5%, what is equivalent to 406 g of pure cocaine.

Qualitative analysis by GC-MS (Agilent 6890-5975)



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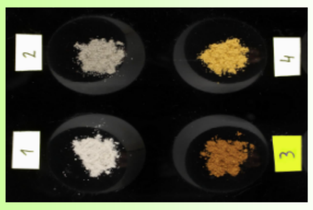
Case 4: CHEMICALLY HIDDEN COCAINE

In the Port of Koper (2008), custom officers examined a cargo, declared as an adhesive/till grout. The cargo consisted of 3217 bags containing: light grey (sample type 1), grey (sample type 2), ocher (sample type 3) and yellow-ocher substance (sample type 4), respectively. For 50 bags, filled with ocher powder (sample type 3), the measured neto weight (5 kg) did not match to declared value of 10 kg. The samples were analysed in the forensic lab. Selected analytical results are shown below:

Presumptive tests		Results (sample type1)	Results (sample type2)	Results (sample type3)	Results (sample type4)
1.	Test on cocaine with cobalt thiocyanate solution	negative	negative	negative	negative
2.	Test on alkaloids with Bertrand's reagent	negative	negative	positive (white precipitate)	negative
3.	Test on halogenide ions with silver nitrate solution	negative	negative	positive (yellow precipitate ⇨possibly iodine ions)	negative



Qualitative analysis

Sample description		Results GC-MS analysis	Results SEM-EDX analysis
1.	Sample type 1	no organic compounds detected	Si, Ca, Al, S, O
2.	Sample type 2	no organic compounds detected	Si, Ca, Ti, Al, K, Fe, O
3.	Sample type 3 (50 bags of net weight à 5 kg)	benzoic acid, cocaine, cocaethylene, benzoylecgonine	Cu, J, K, S, O, C
4.	Sample type 4	no organic compounds detected	Si, Ca, Al, Fe, O

Quantitative analysis

1. **Sample preparation - extraction in $CHCl_3$**
   Determined cocaine concentration (sample type 3) was: **≈ 3 % only.**
2. **Sample preparation - extraction in $CHCl_3$ from alkali water solution, 25 % NH_3.**
   Concentration cocaine in sample type 3 was: **≈ 30 %.**

Summary: During the study of this illicit seizure we obtained some unusual results. Negative presumptive test result with cobalt thiocyanate can be explained by presence of copper ions, which mask the characteristic blue colour development. Based on »false« quantitative determination of cocaine (3%) when extracted in the chloroform; and copper and iodine detection, we presumed that cocaine might have been chemically bonded with copper and iodine into a kind of complex. However, some other explanations can be possible too.

Coca ethylene is usually reported as an ingredient of toxicological samples and is assumed to be an indication of simultaneous abuse of alcohol and cocaine. Recently the possible source of coca ethylene in illicit samples has been highlighted by Casale et. all (Journal of Forensic Sciences 2008;53(3):661-667). They address on new procedure of cocaine base purification (base lavada) with ethanol, coca ethylene is mentioned as a possible by-product obtained by transesterification procedure between cocaine and ethanol.

3. Conclusions

In the first case analyses revealed that a religious statue was made from cocaine-polystyrene solid solution. In the second case we confirmed the presence of cocaine in an oily liquid in hydraulic press. In the next case we detected very pure cocaine, adsorbed on the cotton swabs and hidden in the handmade "cookbook". In the case, where we studied solid mixture which resembled to ceramic adhesive material we assumed that cocaine was most probably chemically bonded with copper and iodine. In that form it can evade detection in field drug tests (based on colour reactions) and laboratory analysis can give wrong cocaine quantitation as well.

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ENFSI DWG MEETING, SLOVENIA, BLED 2010