

Case report

Evidence on unusual way of cocaine smuggling: Cocaine-polymethyl methacrylate (PMMA) solid solution—study of clandestine laboratory samples

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Abstract

An abandoned clandestine laboratory was seized in Slovenia. All confiscated exhibits were analysed in a forensic laboratory, where the following analytical methods were applied: capillary gas chromatography coupled with mass spectrometry (GC–MS) combined also by solid-phase micro extraction (SPME) and pyrolysis (Py) technique, Fourier transform infrared spectrometry (FTIR) and scanning electron microscopy with energy dispersive X-ray detector (SEM–EDX). The most interesting analytical findings can be summarised as follows: at the crime scene some plastic pieces, which contained cocaine dissolved (as solid solution) in polymethyl methacrylate-plexiglass (PMMA), were found. The highest cocaine concentration measured in the plastic sample was about 15% by weight. Two larger lumps of material (12 and 3 kg) were composed mainly of PMMA and CaCO₃ and contained only 0.4 and 0.5% of cocaine, respectively. As for the low cocaine concentration, we assume that those two lumps of material represent discarded waste product—residue after the isolation of cocaine from plastic. Higher quantities of pure solvents (41 l) and solvent mixtures (87 l) were seized. We identified three types of pure solvents (acetone, gasoline and benzine) and two different types of solvent mixtures (benzine/acetone and gasoline/acetone). The total seized volume (87 l) of solvent mixtures holds approximately 395 g of solid residue formed mainly of PMMA and cocaine. Obviously solvent mixtures were used for isolation of cocaine from the plastic. Small quantities of relatively pure cocaine base were identified on different objects. There were two cotton sheets, most probably used for filtration. One sheet had traces of cocaine base (76% purity) on the surface, while cocaine in hydrochloride form (96%) was identified on the other sheet. GC–MS analyses of micro traces isolated from analytical balances showed the presence of cocaine and some common adulterants: phenacetine, lidocaine and procaine. A cocaine sample compressed in the shape of block was also seized. The above analytical findings inferred us to the conclusion that the illicit laboratory was used for the isolation of cocaine from PMMA resin. Further more, analyses confirm that not only isolation but also further manipulation of cocaine, i.e. adulteration/dilution, as well as the formation of cocaine blocks took place in the house. The information obtained through analyses also allowed us to make some hypotheses about possible multistage isolation procedure.

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1. Introduction

There are many ways of cocaine smuggling. When cocaine is transported in commercial vehicles, traffickers conceal the drug in various parts of the vehicle as well as in the cargo. Cocaine has been discovered in airbags, trunks, spare tires, seats and fenders. Some traffickers wrap drugs in smelly things (aromatic coffee, oil, textile softener) in order to mislead drug-

sniffing dogs. Drugs are smuggled in every conceivable stitch of clothing, in the soles of shoes, inserted in body cavities and ingested in balloons. Cocaine bricks have been sealed in a polymeric coating, mixed with charcoal in the cartridge for IBM printers, cocaine has been concealed in hard cover books with hollowed-out compartments in each cover [1]. Besides the methods where cocaine is hidden but exists in the powdered form, smugglers are now using more sophisticated methods, where cocaine is dissolved in various liquid matrices [2,3], used as impregnation [4], mixed with wax [5] or in the form of solid solution in a plastic resin [6]. In such cases, the drug has to be chemically extracted before further marketing or use.

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Extraction procedure usually takes place in a clandestine laboratory. The forensic chemical analyses of evidence from a clandestine laboratory often require much more effort than a simple identification of controlled substance [7]. Identification of sample matrix, solvents, and other non-drug related chemicals, may be just as important as the identification of illicit drug itself [7]. A thorough analysis of the submitted items of evidence can enable a forensic chemist to identify particular smuggling way, to establish possible manufacturing and/or post production method and to demonstrate how a group of items with legitimate uses are being used in manufacturing of an illegal-controlled substance. In some cases, origin of the applied chemicals can be presumed. In addition, by considering the lab equipment seized, the amount of reagents and/or reaction mixtures and starting and/or waste materials available, a yield capability may be estimated in some cases. Since significant health and safety risks can be associated with clandestine laboratories (due to hazardous material that can be found there), identification of chemicals, reaction mixtures and waste products are also important in the framework of appropriate storage or destruction of seized material. Hence, to analyse samples from a clandestine laboratory application of a wider range of analytical methods and/or sample preparation techniques is usually necessary. Many more frequently used methods in forensic investigations are summarised in the work of Ho [8].

In this paper, we present an analytical case study of findings from a clandestine laboratory, which was obviously used for the isolation of cocaine from PMMA resin. Polymethyl methacrylate (PMMA) or polymethyl-2-methylpropanoate is the synthetic polymer of methyl methacrylate. PMMA is an amorphous thermoplastic that can be delivered clear as glass but is also well suited for dyeing. It is freely available on the legal market and is sold under different trade names as for example Plexiglas, Perspex, Acrylite, Acrylplast and Lucite. The material is often used as an alternative to glass. The “glass looks” and the water resistant property of PMMA makes it commonly used for windows, fish tanks, decoration articles, transparent tubes, signs, level glass, etc. It is also used for instance for rear lights of cars and for the spectator protection in ice hockey stadiums. The material is used to produce laserdiscs and sometimes for DVDs, too [9,10]. PMMA has a good degree of compatibility with human tissue so it is also used in medicine (intraocular lenses, bone cement, removable complete dentures, etc.).

2. Materials and methods

2.1. Seized samples

The following background information is necessary to provide an insight into the case. The Slovenian criminal investigators and forensics ransacked a tenement house due to suspicion of cocaine production. On the ground floor a laboratory desk with digital, analytical balances and plastic containers filled with organic solvents as well as original containers of acetone and benzene were found. The main

activity took place on the spacious attic where barrels of different sizes, buckets, vessels, protective masks, kitchen colanders, filters, plastic tubes, four wooden gadgets for mixing, overalls, lab drying apparatus, cotton sheets and many other exhibits were seized. Agglutinated traces and particles of off-white dried material were found almost everywhere, even on the floor and walls. The traces and small particles were hard, fragile. Some larger particles had visible porous structures. Two off-white lumps of porous material, weighting 12 and 3 kg, respectively, were buried outside the house in the garden. Due to the shape of bigger lump (12 kg) we assumed that it represents a hardened sediment (waste plastic), which during the isolation process precipitated at the bottom of a vessel (volume 120 l, ca. diameter 40 cm). It can be estimated from the samples' form and dimension that it was approximately about one half of the waste lump material, which is produced within a single run of an isolation procedure. The bottom part of the lump material showed a partial invert mark of the vessel bottom.

Information on the majority of samples which were analysed in the laboratory is given in Tables 1 (liquid samples) and 2 (solid samples), where samples are grouped together according to their visual properties and, partially, also according to our analytical findings explained later in text. Some liquid containers (see Table 1) were labelled as “PETROL, UN 1203 bencin 90/150”. We should mention here that “bencin” is Slovenian word for automotive gasoline and “Petrol” is Slovenia's largest oil trader which has a network of gas stations over the whole country. Hence, we can conclude that those containers could have been bought in whichever of Petrol's gas stations in Slovenia. Containers labelled as “acetone” were also purchased in Slovenia (that was evident from the labels—details are not given in Table 1).

Table 1
Liquid samples taken from the crime scene

Sample(s) label	Description
5a	7 l of transparent yellow liquid in plastic container (volume of container was 20 l)
5b	0.5 l of transparent liquid in plastic container (volume of container was 20 l, it was originally labelled as “acetone”)
19a	20 l of transparent yellow liquid in a plastic container labelled as “acetone” (volume of container was 20 l)
19b	20 l of transparent yellow liquid in a plastic container labelled as “acetone” (volume of the container was 20 l)
19c	20 l of transparent yellow liquid in a plastic container labelled as “acetone” (volume of the container was 20 l)
1-I	0.5 l of transparent liquid in a plastic container (container volume was 20 l)
3-I	20 l of transparent yellow liquid in a plastic container labelled as “PETROL, UN 1203 bencin 90/150” (container volume was 20 l)
4-I	20 l of transparent yellow liquid in plastic container (container volume was 20 l)
5-I	20 l of transparent yellow liquid in plastic container (container volume was 20 l and it was originally labelled as “PETROL, UN 1203 bencin 90/150”)

Table 2
Solid samples taken from the crime scene

Sample(s) label	Description
A1–A6	Off-white traces ^a (agglomerates) taken from the walls inside six barrels of different volumes (barrels' volumes were: 10, 120, 15, 20, 120, 100 l)
B1–B6	Samples of off-white material found at different locations on the floor. Net weights of samples labelled as B1–B6 were 18.5, 82.8, 16.4, 3.92, 39.8, 4.7 g, respectively
C	30.22 g of off-white material in 50 l plastic bucket
D1–D4	Off-white traces ^a on wooden gadgets (four gadgets were found—length of single gadget was 90 cm)
E1–E3	White traces ^a inside two pieces of plastic tubes (labelled as E1 and E2) of 1.5 m length and diameter of 1.4 cm. Off-white traces ^a inside plastic tube (E3) of 2 m length and diameter of 1.8 cm
F1–F3	Off-white traces ^a (F1), black (F2) and white traces ^a (F3) inside the barrel of 35 l volume
G	White traces ^a on the walls of 70 l barrel
H1 and H2	White traces ^a on the walls of two 100 and 70 l barrels
I	White traces ^a on the white sheet
J	White traces ^a on the white sheet
K1 and K2	Off-white lumps of porous material found outside the house—in the garden, covered with soft soil. Net weights of samples K1 and K2 were 12 and 3 kg, respectively. The lump of sample K1 was a half-cylinder shaped piece with 40 cm diameter and 18 cm high
L	380 g of white material, compressed in the shape of block, dimension 15 cm × 10 cm × 2 cm (found in attic under wood panels)
M1–M5	Micro traces taken from four pieces of analytical balances and from laboratory desk

^a The term traces denotes samples with nett weight from 0.1 to 0.5 g.

2.2. Chemicals

Cobalt (II) thiocyanate (Co(SCN)₂) applied for the preparation of Scott's reagent [11] was from Sigma–Aldrich, barium chloride-2-hydrate (BaCl₂·2H₂O) and silver nitrate (AgNO₃) for screening tests on sulphate and chloride ions, were obtained from Kemika, Zagreb. Tungstosilicic acid monohydrate (H₄[Si(W₃O₁₀)₄]·H₂O) for screening test on alkaloids (also known as Bertrand's reagent) [12], potassium bromide (KBr) for FTIR sample preparation and nonadecane (C₁₉H₄₀) applied as an internal standard for cocaine quantitation, were from Merck. Cocaine base standard reference material (99.51%) and cocaine hydrochloride standard reference material (99.89%) were purchased from Lipomed. PMMA granulate was kindly provided by Institute of Chemistry (Ljubljana, Slovenia). All other chemicals and solvents used were analytical reagent grade or better.

2.3. Presumptive tests

The presence of alkaloids was tested by 5% water solution of H₄[Si(W₃O₁₀)₄]·H₂O (Bertrand's reagent). The Scott's colour test was used for presumptive identification of cocaine. Water solutions of barium chloride BaCl₂ (1 M) and silver nitrate AgNO₃ (0.1 M) were applied as screening tests for sulphate and chloride ions, respectively.

2.4. Instrumental analyses and sample preparation

Due to chemical diversity and complexity of seized exhibits, several analytical methods were applied. Identification of some organic ingredients and quantitation of cocaine was achieved by tandem GC–MS, which is usually applied for the analyses of bulk drug samples [13]. Extraction/concentration of solvent residues trapped in different matrices was accomplished by a well-known solid-phase micro extraction (SPME) [14] followed by GC–MS analyses. Pyrolysis system (Curie point) in combination with GC–MS, which is frequently applied in polymers studies [15,16], enabled us to identify plastic ingredients of seized samples. Besides chromatographic methods also Fourier transform infrared spectrometry FTIR, which can give some important additional information on illicit drug samples (identification of drug form—base or salt, differentiation between polymorphic modifications, identification of some organic as well as inorganic impurities) [17], is routinely used in our laboratory. In this particular case scanning electron microscopy–energy dispersive X-ray system (SEM–EDX) was also applied for elemental analyses of some samples. Details on the applied methods are given below.

2.4.1. Gas chromatography mass spectrometry (GC–MS)

2.4.1.1. GC–MS qualitative and quantitative analyses. Qualitative and quantitative analyses were performed on an HP 5890 capillary gas chromatograph equipped with a mass selective detector (MSD) HP 5972 and an auto sampler. Injection volume 1 μl and split mode (20:1) operation were chosen. Agilent's split inlet liner (part number: 19251-60540) was applied. A chromatographic separation was achieved on an HP1-MS (100% dimethylpolysiloxane) capillary column (length 30 m, ID 0.25 mm, film thickness 0.25 μm). The carrier gas was helium at a flow rate of 1.2 ml/min. The oven temperature program was: 150 °C for 1 min, followed by heating up to 240 °C with a rate of 10 °C/min, held for 4.5 min, then heated at 17 °C/min increments up to 290 °C and, finally, 14 min isothermal. The injector and GC–MS interface temperatures were set to 280 and 300 °C, respectively. The column effluent was directed into the ion source of MSD where molecules were ionized by electrons (energy 70 eV). For qualitative analyses, mass spectra were scanned in the range from 40 to 450 amu, while for the quantitative determination of cocaine a selected ion-monitoring mode (SIM) acquisition was applied. For cocaine, the ion of *m/z* 303 and for internal standard (nonadecane, C₁₉H₄₀) ion of 57 *m/z* was scanned.

2.4.1.1.1. Sample preparation. For qualitative GC–MS analyses, solid samples were dissolved in chloroform. Insoluble parts of samples were removed by centrifugation and/or filtration when necessary. In some cases (indicated in Section 3), insoluble part was further analysed by FTIR, SEM–EDX or Py-GC–MS. Liquid samples were partially evaporated and diluted by chloroform and analysed.

For quantitative determination of cocaine from approximately 1–10 mg, accurately weighted samples were dissolved in 1 ml of chloroform with 0.5 mg/ml C₁₉H₄₀ as an internal standard. For quantitation of cocaine in liquid sample, the known

volume of liquid was evaporated to dryness and later solid residue was redissolved in 1 ml of chloroform with $C_{19}H_{40}$ as internal standard. If the obtained analytical result was outside the calibration range, the sample was prepared and measured again. Sample weight (or volume for liquid samples) was adjusted appropriately—so that the obtained result was within the calibration range.

Cocaine calibration solutions were prepared by dissolving appropriate amounts of cocaine base (Lipomed) in 1 ml chloroform with 0.5 mg/ml nonadecane ($C_{19}H_{40}$) as internal standard. Five-point calibration, for the concentration range from 0.2 to 1.0 mg/ml, was performed.

2.4.1.2. Pyrolysis and SPME analyses. Pyrolysis and analyses of exhibits sampled by SPME were performed on an HP 5890 capillary gas chromatograph interfaced with a mass selective detector (MSD) HP 5971. MSD operational parameters and helium flow rate were set to the same values as described for the instrument above (Section 2.4.1.1). The non-polar column (HP1-MS) was applied. For pyrolysis, Curie point flash pyrolyser (Pyromat GSG—with an auto sampler) was connected to the injection port of the gas chromatograph. A pyrolyser head temperature was set to 150 °C. The solid sample (approximately 5 µg) was placed inside a ferromagnetic sample carrier (with a Curie point of 764 °C) and pyrolysed for 10 s. The products were swept into the gas chromatograph where they were resolved and later identified by MSD. The column heating temperature program was set as follows: 100 °C for 1 min, increased to 220 °C at a rate of 10 °C/min, hold for 2 min, heating up to 300 °C at a rate of 30 °C/min and then held for 10 min. GC was operated in splitless mode, while MSD operating parameters were described above. In the injection port of GC, Agilent's splitless liner (part number P/N: 5062-3587) was applied.

For SPME analyses, the injection port was equipped with a unit that enables insertion of SPME fiber into the injector of GC. After the thermal desorption from the fiber, analytes were resolved in GC and identified by MS. The injection port temperature was set to 250 °C and the column heating temperature program was set as follows: 45 °C for 2 min, increased to 220 °C at a rate of 10 °C/min, held for 2 min, heated up to 300 °C at a rate of 30 °C/min and then held for 10 min.

GC was operated in splitless mode (with Agilent's splitless liner—part number 18740-80220), while MSD operating parameters were described above.

2.4.1.2.1. SPME—sample preparation. About 1–2 g of solid sample or a drop of liquid, was inserted into 20 ml glass vial, which was tightly capped with a rubber cap. SPME fiber coated with 75 µm Carbovax (mounted into the fiber holder 5-7330, Supelco, for manual use) was inserted through the cap. The sampling time was 20 min at temperature 45 °C.

2.4.2. FTIR spectrometry

FTIR spectra were collected using an instrument Perkin Elmer Spectrum 2000 equipped with a KBr beam splitter and a DTGS (deuterated triglycerine sulfate) detector. For each measurement three scans for background and three scans for

sample were collected, respectively, in the wavenumber range from 400 to 4000 cm^{-1} .

2.4.2.1. FTIR sample preparation. FTIR was applied for analyses of solid samples, for identification of solid precipitate from liquid samples (obtained after adding the hexane) and for identification of inorganic part of solid samples. Inorganic parts of samples were obtained by thermal decomposition of samples, i.e. organic material has been destroyed by combustion before analysis. This was done by taking approximately 2 g of sample in a silica crucible and placing it over a flame of a Bunsen burner. When reducing to ashes was completed (approximately 5 min), the residue was isolated and KBr pellet prepared.

To prepare KBr pellets, about 2 mg of sampled material was ground gently together with about 200 mg of KBr. The pellets were pressed at high pressure (60 000 N/m^2) to produce disks about 1 mm thick and 12.7 mm in diameter. Each sample was measured shortly after preparation, to avoid water being absorbed into the KBr disc.

2.4.3. SEM–EDX

SEM–EDX spectra were obtained by a CAM SCAN CS 24 scanning electron microscope and an OXFORD INCA energy dispersive X-ray spectrometer. The accelerating voltage was 20 kV.

2.4.3.1. SEM–EDX sample preparation. A double-sided adhesive tape, affixed to an aluminium SEM stub, was used for a SEM–EDX sample preparation. The tape was lightly pressed on the inorganic part of the sample powder. Inorganic parts of samples were obtained by a thermal decomposition of samples (procedure has already been described in Section 2.4.2).

3. Results

3.1. Liquid samples

The seized liquids were tested by various micro chemical tests, followed by instrumental analyses. Results are presented in Table 3. Bertrand's reagent was applied for detection of alkaloids, while screening on Cl^- and SO_4^{2-} ions were performed by $AgNO_3$ and $BaCl_2$, respectively. Since the reaction with $BaCl_2$ was negative for all liquid samples, the results are omitted from Table 3. The presence of chlorine was confirmed as well by SEM–EDX analyses of thermally decomposed sample's solid residue, obtained after the evaporation of organic solvents.

When samples were diluted with hexane or water (we tested samples for miscibility with different solvents), traces of white material almost instantly precipitated from some liquids (see Table 3). FTIR analyses enabled us to identify the white precipitate as PMMA. An example of a result obtained by the FTIR analysis is given in Fig. 1, where FTIR spectra of the white precipitate (of sample 5a) and PMMA standard are shown.

Table 3
Collected results of liquid samples

Tests and methods		Micro chemical tests addition of hexane (or water)			Instrumental analyses				Solid residue after evaporation of solvents g/l and (as wt.%)	Volume ratio of solvents acetone/benzine or acetone/gasoline
Sample label	Volume (l)	Bertrand test on alkaloids	AgNO ₃ test on Cl ⁻ ions	Precipitate after addition of water	GC–MS and SPME-GC–MS (qualitative)	GC–MS cocaine concentration g/l and (as wt.%)	FTIR of white precipitate	Py-GC–MS of white precipitate (qualitative)		
5a	7	+	+	White precipitate	Acetone, benzine, cocaine	2.4 (0.25)	PMMA	PMMA	6.7 (0.7)	75:25
5b	0.5	–	–	–	Acetone	–	Not measured	Not measured	Not measured	Pure solvent
19a	20	+	+	White precipitate	Acetone, benzine, cocaine	0.3 (0.04)	PMMA	PMMA	5.8 (0.6)	75:25
19b	20	+	+	White precipitate	Acetone, benzine, cocaine	0.3 (0.04)	PMMA	PMMA	5.8 (0.6)	75:25
19c	20	+	+	White precipitate	Acetone, benzine, cocaine	0.48 (0.06)	PMMA	PMMA	2.9 (0.3)	75:25
1-I	0.5	–	–	–	Benzine	–	No precipitate	No precipitate	Not measured	Pure solvent
3-I	20	+	+	White precipitate	Acetone, gasoline cocaine	0.2 (0.03)	PMMA	PMMA	2.9 (0.3)	65:35
4-I	20	–	–	White precipitate	Gasoline	–	Not measured	PMMA	1.9 (0.2)	Pure solvent
5-I	20	–	–	–	Gasoline	–	No precipitate	No precipitate	Not measured	Pure solvent

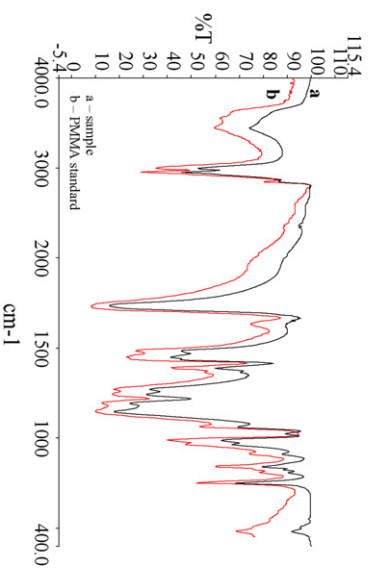


Fig. 1. FTIR spectrum of precipitated white material of sample 5a (spectrum a) and comparative spectrum of PMMA standard (spectrum b).

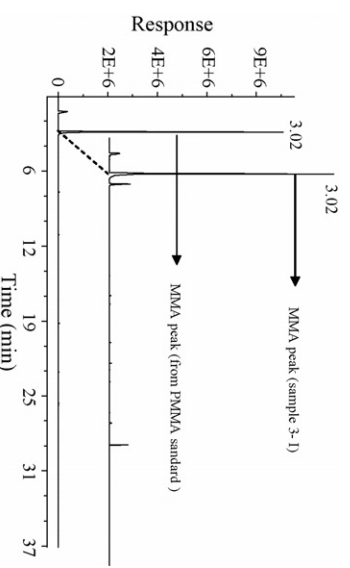


Fig. 2. TIC chromatograms of precipitated white material (sample 3-I) and PMMA standard—results obtained by Py-GC–MS.

FTIR results were confirmed also by Py-GC–MS. Fig. 2 shows the pyrograms of PMMA reference material and the pyrogram of the white precipitate of the sample 3-I. Based on the characteristic mass spectrum (see Fig. 3) the main pyrolysis product of PMMA reference material was identified as methyl methacrylate monomer (MMA). Such a result was expected, since PMMA tends to depolymerise mostly (>90%) into an original monomer at the temperatures above 500 °C [18].

GC–MS analyses of liquid samples enabled us to separate and identify cocaine and gasoline or benzine (see Fig. 4). With the applied procedure, acetone could not be detected, due to its short elution time. Hence, the SPME sampling of a vapour phase over the investigated liquids followed by GC–MS

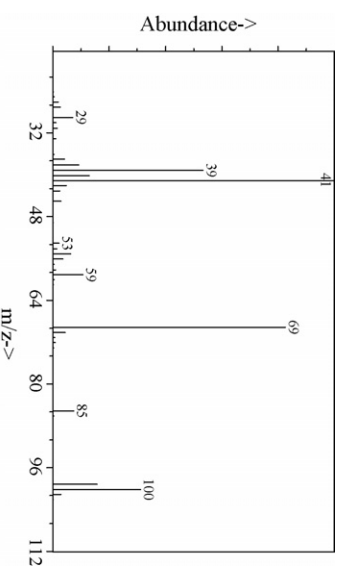


Fig. 3. Mass spectrum of main pyrolysis product of PMMA (retention time at 3.02 min).

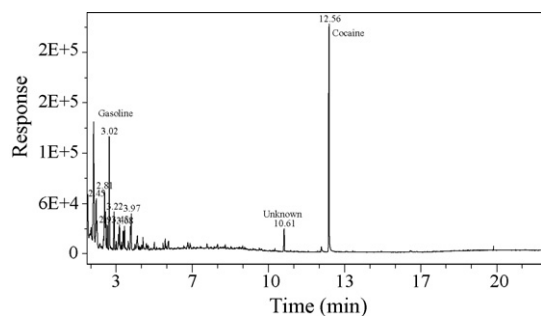


Fig. 4. TIC chromatogram—analysis of 1 μ l partially evaporated and diluted liquid sample 3-I.

analyses was applied for the identification of acetone. With the same procedure the presence of gasoline or benzene were also confirmed. Examples are given in Figs. 5 and 6.

Table 3 shows that liquid samples can be divided into five distinct groups. There are three types of *pure solvents* (acetone, gasoline and benzene) and two different types of *solvent mixtures* (benzene/acetone and gasoline/acetone). All solvent mixtures hold a small amount of illicit drug cocaine (from 0.2 up to 2.4 g/l), plastic PMMA and Cl^- ions. From data shown in Table 3 it can be calculated that total seized volume (87 l) of *solvent mixtures* holds approximately 395 g of solid residue (data obtained by evaporation of solvents) formed mainly of PMMA and cocaine. We calculated from measured cocaine concentrations (see Table 3) that the seized solvent mixtures (87 l) contain approximately 42 g of cocaine.

We estimated acetone/gasoline and acetone/benzene volume ratios in samples 5a, 19a, 19b, 19c and 3-I. The following procedure was applied. We prepared two sets of standard solutions where acetone/gasoline and for second set acetone/benzene were mixed in known volume ratios, starting from volume ratio 10% of acetone to 90% of gasoline (benzene) and ended at ratio 90–10% for acetone and gasoline (benzene), respectively. At applied volume ratios, acetone and gasoline were completely miscible (a single-phase system). A quantity of 6 ml of each solution was mixed with 3 ml of water. After the addition of water, we obtained a two-phase system. The upper layer was a gasoline-rich phase while the bottom layer was water-rich phase. Since acetone is more soluble in water than in gasoline, the volume of water-rich phase is increased as the

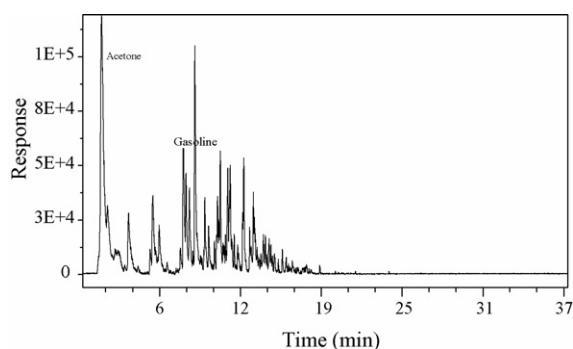


Fig. 5. Total ion chromatogram of the vapour phase over the sample 3-I (SPME technique).

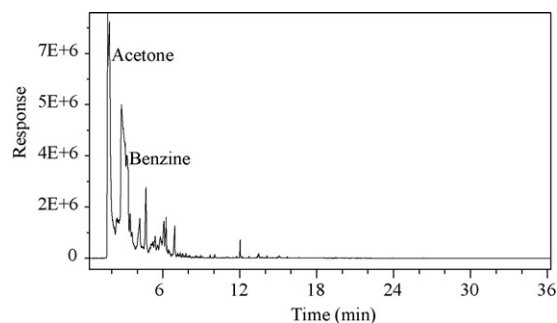


Fig. 6. Total ion chromatogram of the vapour phase over the sample 19a (SPME technique).

portion of acetone in the solvent mixture is increased. The calibration graph, where the volume of water-rich phase (bottom layer) is shown as a function of volume fraction of acetone in acetone/gasoline (or acetone/benzene) mixture, was constructed and is shown in Fig. 7. To evaluate the composition of seized solvent mixtures, we mixed 6 ml of each seized liquid sample with 3 ml of water. After equilibration and phase separation, the volume of water-rich phase was established and the volume ratio of solvents was deduced from the calibration graph. The assessed error of determined volume ratios is $\pm 2.5\%$ (absolutely).

3.2. Solid samples

Analytical results for solid samples are collected in Table 4. Quantitative results for cocaine are presented for each sample, other data refer to all samples of the same type. Analytical findings are summarised according the sample type. The comments are given below.

3.2.1. Off-white samples

FTIR analyses show that all *off-white samples* (A1–A6, B1–B6, C, D1–D4, E3, F1, K1 and K2) are composed of PMMA plastics (spectra were similar to that shown in Fig. 1) and some inorganic salts. The presence of PMMA was confirmed also by Py-GC–MS (see Fig. 8). FTIR analyses of inorganic part of samples (residual after thermal decomposition of sample) revealed that all samples contain CaCO_3 and CaSO_4 . There was a significant difference in CaSO_4 content among off-white

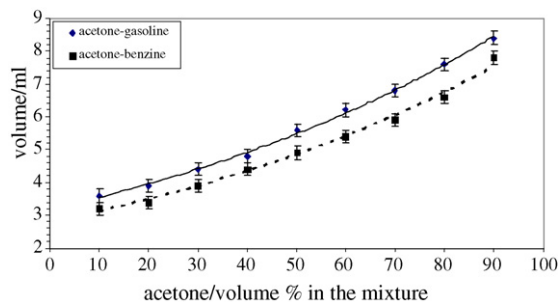


Fig. 7. Calibration graph—volume of water-rich phase as a function of volume fraction of acetone in acetone/gasoline (or acetone/benzene) mixture.

Table 4
Collected results of solid samples

Samples	Cocaine (%)	PMMA by FTIR and Py-GC-MS	FTIR inorganic salts	SEM-EDX (Ca, S, Cl)	SPME-GC-MS (residual solvents)
A1–A6	5.5; 2.5; 12.5; 15.0; 7.3; 10.1	+	CaCO ₃ , CaSO ₄	Ca, S, Ti, Mg, Si	Acetone, gasoline
B1–B6	3.2; 1.5; 4.5; 3.5; 2.7; 3.0	+	CaCO ₃ , CaSO ₄	Ca, S, Ti, Mg, Si	Acetone, gasoline
C	2.7	+	CaCO ₃ , CaSO ₄	Ca, S, Ti, Mg, Si	Acetone, gasoline
D1–D4	6.0; 6.0; 2.0; 2.0	+	CaCO ₃ , CaSO ₄	Ca, S, Ti, Mg, Si	Acetone, gasoline
E1 and E2	3.0; 3.0	+	(NH ₄) ₂ SO ₄	S, Cl	Acetone, gasoline
E3	2.7	+	CaCO ₃ , CaSO ₄	Ca, S, Ti, Mg, Si	Not measured
F1	7	+	CaCO ₃ , CaSO ₄	Ca, S, Ti, Mg, Si	Acetone, gasoline
F2	16	+	Not measured	–	Acetone, gasoline
F3	–	–	(NH ₄) ₂ SO ₄	S	Not measured
G (6 cm)	82	–	–	Not measured	Not measured
G (21 cm)	79	–	–	Not measured	Not measured
G (28 cm)	40	–	CaCO ₃ , CaSO ₄	Not measured	Not measured
H1	66 (as% of HCl form)	–	–	Cl	Acetone
H2	71 (as% of HCl form)	–	–	Cl	Acetone
I	76	–	CaCO ₃ (traces), CaSO ₄ (traces)	–	–
J	96 (as% of HCl form)	–	–	Cl	Acetone
K1	0.4	+	CaCO ₃ , CaSO ₄ (traces)	Ca, (S), Ti, Mg, Si	Acetone, gasoline
K2	0.5	+	CaCO ₃ , CaSO ₄ (traces)	Ca, (S), Ti, Mg, Si	Acetone, gasoline
L ^a	56 (as% of HCl form)	–	–	Cl	Acetone
M1–M5 ^b	Not measured	–	Not measured	Cl	Not measured

Comment: plus or negative sign means positive or negative reaction/detection.

^a Sample L: the presence of lidocaine was confirmed as well by GC-MS.

^b Samples M1–M5: the presence of phenacetine, lidocaine and procaine was confirmed as well by GC-MS.

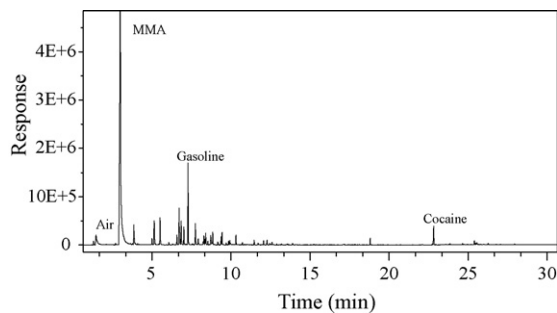


Fig. 8. TIC chromatogram of sample K1 (12 kg lump)—result of Py-GC-MS.

samples seized inside the house (see Fig. 9) and two lumps of material K1 and K2, which were found outside the house. Samples K1 and K2 contained only micro traces of CaSO₄ (see Fig. 10).

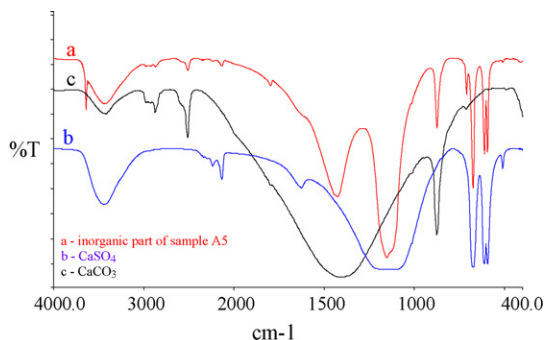


Fig. 9. FTIR spectrum of inorganic part of sample A5 and comparative spectra of CaCO₃ and CaSO₄.

The elemental composition of inorganic ingredients of samples was studied also by SEM-EDX. Spectra of two typical off-white samples, seized inside the house, are shown in Fig. 11, while spectra for samples K1 and K2, seized in the garden, are shown in Fig. 12. We can see that a major difference among samples is in the sulphur content. SEM-EDX findings are consistent with FTIR results, where only traces of CaSO₄ were found in samples K1 and K2, while other off-white samples contained significantly larger amount of CaSO₄. Traces of Ti, Mg and Si were detected in all samples. We believe traces of these elements originate as foreign matters in CaCO₃ or limestone [19].

Using SPME-GC-MS, residuals of occluded solvents were investigated. Acetone and gasoline were detected in all off-white plastic samples seized inside the house.

The quantitative analyses show that the amount of cocaine captured in plastic samples, which were found inside the house, ranged from 1.5 up to 15%, the latter being the highest

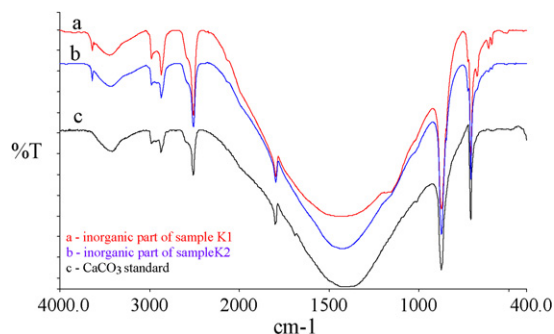


Fig. 10. FTIR spectra of inorganic parts of samples K1 and K2 and comparative CaCO₃ spectrum.

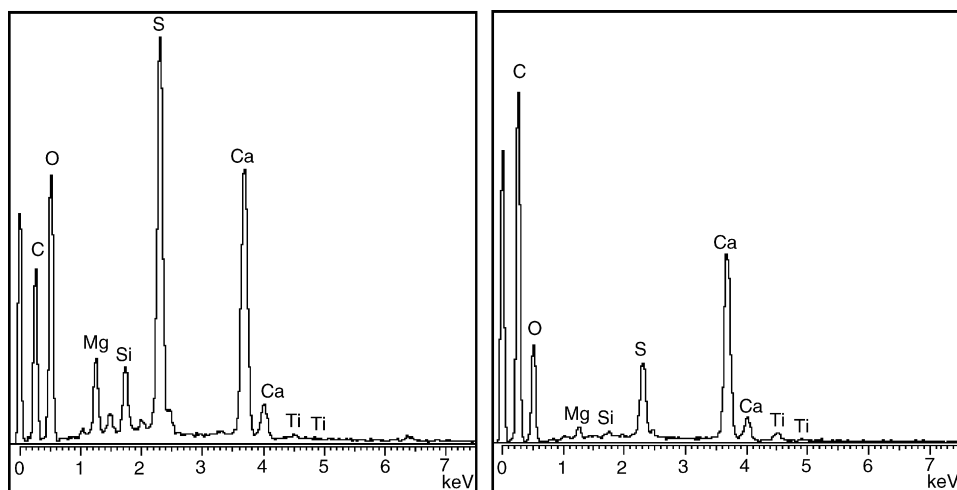


Fig. 11. X-ray spectra of two typical off-white samples, seized inside the house.

value found. Two lumps (K1 and K2) of discarded plastic material, found outside the house, contain only 0.4 and 0.5% of cocaine, respectively. The estimated error in the cocaine quantitation, expressed in the term of relative standard deviation (R.S.D.) is $\pm 5\%$.

As for the low cocaine concentration, lumps K1 and K2 undoubtedly represent discarded waste product, which remained after the isolation of cocaine from plastic. Other agglomerates of off-white samples (found in the house) most probably persisted on different objects accidentally—as remainders during the isolation procedure.

3.2.2. White traces

Table 4 reveals that several samples consisted of white traces containing relatively pure cocaine. We did not detect a PMMA in those samples. White traces of a sample G (barrel sampled at a height of 6, 21, 28 cm, respectively) contain 82, 79 and 40% cocaine base. The cocaine base concentration was dependant on the sampling height. A cocaine base was detected also on one of the white sheets (sample I). The average purity of traces sampled from the sheet was 76% (as cocaine base) by weight, and the rest of the sample was

CaCO_3 and CaSO_4 . Samples H1, H2 and J contain high purity cocaine hydrochloride, i.e. 66, 71 and 96%, respectively (expressed as concentration of cocaine HCl form). Samples H1, H2 and J inferred to the idea that the desired final product was most probably cocaine hydrochloride.

3.2.3. Other samples

White, crystalline, water-soluble material (sample F3) from one bucket was analysed by FTIR and identified as NH_4SO_4 . In the same bucket, black material (sample F2), insoluble in organic solvents and in water, was also found. Sample F2 is most probably activated carbon. We proved that 16% of cocaine was absorbed on that material. Traces of NH_4SO_4 , PMMA and cocaine (3%) were detected also inside two of the three plastic tubes (E1 and E2), while one tube (E3) was contaminated with off-white traces-plastic (for analytical results see Table 4). GC–MS analyses of micro traces isolated from analytical balances and from the desk (M1–M5) showed the presence of cocaine and some common adulterants: phenacetine, lidocaine and procaine. The presence of lidocaine was confirmed as well in a cocaine block (L). Higher quantities of pure adulterants were not found on the crime scene.

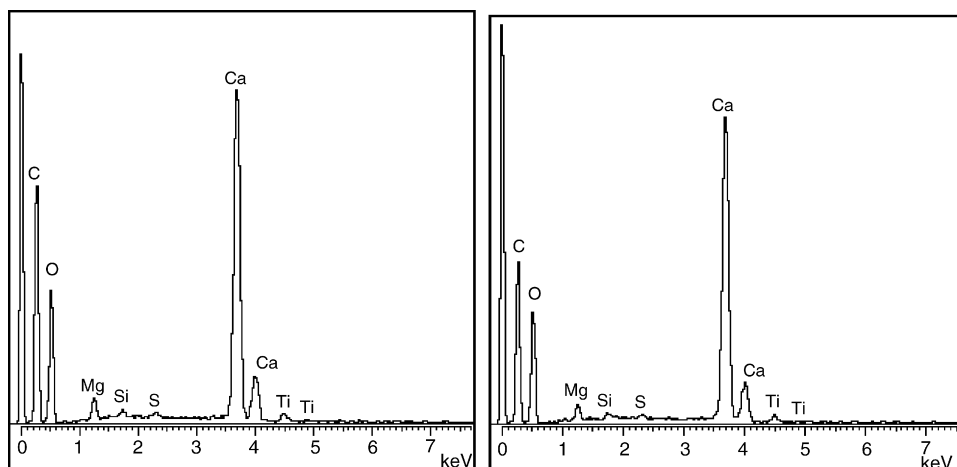


Fig. 12. X-ray spectra of samples K1 and K2.

4. Discussion

The analytical findings described above inferred us to the conclusion that the illicit laboratory was used for the isolation of cocaine from PMMA resin. Cocaine-PMMA plastic material can be obtained with different procedures. In general, cocaine can be added before the polymerization step (for example into the solution of polymer in monomer syrup) or can be mixed with already prepared amorphous PMMA and then formed (here again different procedures are possible) into objects of different shapes. Detailed explanations of many different possibilities for the cocaine-PMMA plastic preparation are beyond the scope of this paper.

In our case, we can suppose that a starting cocaine-plastic solid solution contained more than 15% of cocaine, which was the highest concentration determined in the investigated off-white cocaine-plastic samples. In the single comparable report (that we found) on dog kennels made from cocaine-plastics [6] the reported cocaine concentration in the plastic was 30.4%. Unfortunately, in our case, neither the shape nor the exact composition and quantity of starting material are known. Anyway, judging from the dimensions of the seized vessels and the volume of liquids and waste plastic material found at the crime scene, we could at least imagine the dimension of production. If we suppose that the starting material contained between 15 and 30% of cocaine, we can roughly estimate that the cocaine yield (based on the sum of weights of lumps K1 and K2) should be between 2.5 and 6.5 kg. Having in mind the shape of the sample K1 (it is approximately a half of cylinder shaped piece) we can estimate that the quantity of waste material should be at least approximately 24 kg, what rise the potential cocaine yield up to 10 kg. An estimate of the financial value of the product can be evaluated from UNDCP data (for Europe). In the year 2004 average price of cocaine at street level was € 71 g⁻¹ and for wholesale level € 37 g⁻¹ [20].

We presume that the isolation of cocaine from PMMA was a multi-step procedure, where some steps might have been repeated several times (see Fig. 13). Due to an abundance of missing data, some additional experimental work is necessary (and is already going on) to provide us with a better insight into the possible isolation procedure, which can be highly dependant on the composition of starting material. The main question is about CaCO₃ (which represents about 30% of waste plastic material): “Is it possible that CaCO₃ was present in the starting material?” We believe that the answer is yes, since CaCO₃ is widely used as a filler in many industrial plastics [21,22]. Anyhow, the first isolation step undoubtedly involved dissolution of PMMA-cocaine or PMMA-cocaine-CaCO₃ plastic material. We presume that acetone might have been applied as a solvent in our case, since PMMA shows an excellent solubility in acetone [23] and higher quantities of this solvent were found at the crime scene. In our opinion the procedure described by Goldfarb (extraction of cocaine from PMMA plastic was compared by extraction of cocaine from coca leaves), where dilute hydrochloric acid supposedly used for extraction is less probable, since PMMA shows good resistance (7 days at room temperature) to hydrochloric acid

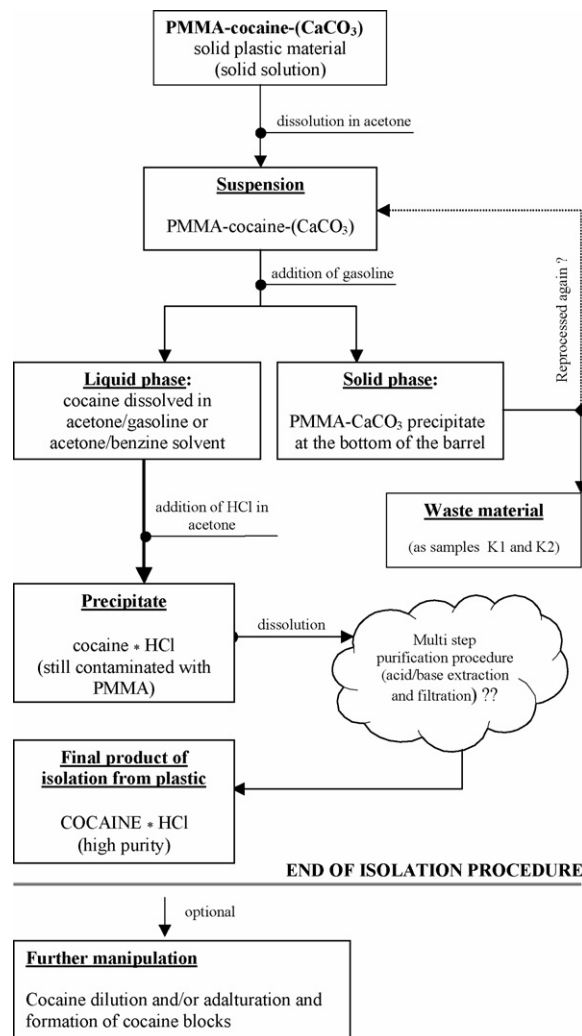


Fig. 13. The possible multi-step procedure for isolation of cocaine.

(HCl ≤ 37%) [23]. After the dissolution of cocaine-plastic in acetone, dissolved cocaine and plastic had to be separated. We assume that gasoline (or benzine in additional purification step) was added to acetone at this stage. Adding gasoline (or benzine) limits the solubility of PMMA, while cocaine is freely soluble [24]. PMMA (or PMMA-CaCO₃ when CaCO₃ is present in the starting material) precipitates and sits at the bottom of the vessel. After a while, material becomes hardened and takes the shape of the bottom part of the vessel. The results of our preliminary simulations showed that when CaCO₃ is present in starting material PMMA and CaCO₃ form homogeneous precipitate—visually very similar to samples K1 and K2. After the separation of precipitate and liquid phase (tubes might have been used for this procedure), cocaine was probably precipitated from the organic acetone/gasoline layer as cocaine hydrochloride. This can be achieved by adding a hydrochloric acid–acetone mixture to the acetone/gasoline phase. The composition of solvent mixtures (all of them contain Cl⁻ ions) support this idea. Further processing is not quite clear but we presume that the first cocaine hydrochloride product (most probably still slightly contaminated with PMMA) was additionally purified in a multi-step procedure which involved

dissolution, followed by acid–base extractions, filtrations through the sheets, as well as the purification on active carbon, which was also found among samples. We assume that ammonium sulphate traces, which were found among samples, might have been applied within the purification process. With the procedure described above, we could not explain the presence of sulphate traces in the plastic waste product. Was it the contaminant or were there some additional steps involved in the isolation procedure?

We can conclude from the obtained analytical data that the desired final product of isolation procedure was cocaine hydrochloride of high purity—with no plastic material present. A sample J confirm this. Traces from analytical balances, laboratory desk and the sample of a cocaine block do not only show the isolation from PMMA matrix but also indicate a further manipulation of cocaine i.e. adulteration/dilution as well as the formation of cocaine blocks took place in the house. Someone can ask: “Why first to remove one matrix and prepare high purity sample and than dilute it?” In our case, the answer is simple. Cocaine-plastic material is a clever solution for smuggling cocaine through the border control. However, due to its properties, cocaine-plastic cannot be used for sniffing, injection or smoking (and in our opinion could hardly be even sold as cocaine since it looks and behaves differently). Hence, to obtain “normal” cocaine properties – plastic have to be removed completely – and the result is cocaine of high purity. Then cocaine can be sold pure or can be diluted with appropriate substances (which do not change usability or visual and physical properties of cocaine much) and sold afterwards. The aim of this dilution is to increase the weight of material—to get more money for it.

5. Conclusions

Analytical findings obtained during the case study inferred us to the conclusion that the illicit laboratory was used for the isolation of cocaine which was smuggled as a plastic-cocaine solid solution. Plastic material was identified as PMMA. Due to the lack of data, some additional experimental work is necessary to get a better insight into the possible isolation procedure, which can be highly dependant on the composition of starting material. Anyway, the information obtained by analyses allowed us to make some hypotheses about the possible multi-stage isolation procedure. Some analytical findings confirm that not only the isolation but also further manipulation of cocaine, i.e. adulteration and/or dilution took place in the investigated crime scene.

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