Toxichem Krimtech 2011;78(Special Issue):200

Smoke analysis of adulterated illicit drug preparations

Evelyn Pawlik[1], Hellmut Mahler[2]

[1]Universitätsklinikum Düsseldorf, Institut für Rechtsmedizin, Forensische Toxikologie, Moorenstraße 5, D-40225 Düsseldorf
[2]Landeskriminalamt NRW, Kriminalwissenschaftliches und -technisches Institut, D-40221 Düsseldorf, Germany. hellmut.mahler@polizei.nrw.de

Key words: adulterants, effect amplifiers, smoking, marijuana, cocaine, amphetamine

Abstract

Aim: During the last decade the common adulterants for illicit drug mixtures have changed. Formerly, sugars and sugar alcohols dominated cutting agents for marijuana, cocaine preparations and amphetamines. Nowadays, adulterants in powder drugs are predominantly additional active substances or effect amplifiers (see below). In marijuana samples at the LKA NRW, sugars and sugar alcohols, food hemp, glass powder, sand, talc, hair spray, nitrate- and phosphate-containing fertilizers as well as neem oil could be detected in single cases. Elsewhere lead, synthetic resin, spices and edible oils as well as "Brix" were claimed to be found. We examined the influence of the cutting agents for the preparation of crack and freebase and their pyrolysis properties, in a specially adapted smoking apparatus. Due to reports about marijuana samples with fertilizers (up to 50 % weight) that cause acute respiratory syndromes, these materials were likewise tested.

Material and methods: Representative illicit drug preparations from seizures in NRW were used. Examinations were mainly done by scanning electron microscopy, light microscopy, X-ray diffraction, ion and gas chromatography as well as HPLC-TOF-MS.

Results and discussion: In the smoke of marijuana adulterated with fertilizers high fractions of nitrogen oxides were found - a possible explanation for respiratory effects.
Amphetamine sulphate salts adulterated with caffeine and 4-fluoroamphetamine were checked for smoking. Merely caffeine and 4-fluoroamphetamine were detected in relevant amounts. Cocaine preparations adulterated with lidocaine, procaine, diltiazem, hydroxyzine, levamisol, caffeine and phenacetin were converted to crack and freebase samples, analyzed and then smoked in suitable apparatus. The smoke gases were condensed and analyzed. The production of freebase and crack may eliminate sugar and sugar alcohols, but all other cutting substances were present in the cocaine base preparations. In the smoke these cutting substances were detected in similar fractions. Phenacetin, lidocaine, procaine and diltiazem showed the best recovery. Toxicological effects for the lung are discussed.

Conclusion: The examined adulterants in amphetamine or cocaine preparations, caffeine, 4-fluoroamphetamine, phenacetin, hydroxyzine, diltiazem, lidocaine and procaine as well as fertilizers (on marijuana samples) can be inhaled via smoking, since they were found in the smoke condensates in sufficient amounts.

1. Introduction

The abuse of drugs like cocaine, amphetamine and marijuana causes various toxic effects predominantly on the cardiovascular-system [1] and the brain (e.g. cerebral infarct). But not only the drugs themselves are carrier of serious risk for the health, just as the adulterants within the illegally traded drug preparations. During the last decade cutting agents typically used for illicit drug mixtures have changed. In the past, sugar and sugar alcohols were predominantly

used for the cutting of amphetamine, cocaine and marijuana. Today powder drugs like cocaine and amphetamine were adulterated with active substances or effect amplifiers like the local anesthetics lidocaine, procaine, benzocaine and tetracaine, the psychoactive stimulantes caffeine, phenacetin and 4-fluoroamphetamine, the anthelminthic levamisole, the antihistamine hydroxyzine, and the calcium channel blocker diltiazem, as well as various other substances. In addition to the above mentioned cutting agents for hemp products, some marijuana samples examined by the LKA NRW contained glass powder, food hemp, sand, talc, hair spray, nitrate- and phosphate-containing fertilizers as well as neem oil. Elsewhere lead [2] was detected and synthetic resin, spices and edible oils as well as a product named "Brix" (the internet reference describes it as synthetic liquid with e. g. sugar and “liquid polymer”, that shall be prepared “especially for the adulteration of marijuana”) were claimed to be found [3][i]. However products with the name “Brix” (described to contain carbohydrates, amino acids and vitamins) are sold as plant boosters, that are claimed to transport nutritive either by soil or directly via the leaf into the plants. Leaf fertilisation is a method that may work for water soluble compounds e. g. inorganic salts and in limited manner for small organic molecules like sugars. Maybe the use of “Brix” 7 to 10 days prior harvest is due to a misunderstanding or a wrong handling of plant growth products and the finding of “liquid polymer” due to a presence of starch.

Adulterants or cutting agents are mainly used to increase the weight to develop sales. Sometimes impurities accidentally attain a product e.g. during a bad done synthesis or they even might be added deliberately. Therefore, cocaine consumers claim to reach a cleansing effect by transforming their cocaine hydrochloride preparations into the freebase for smoking, which is more effective to a so called “flash”. Thus, the examination of cleansing effects of cocaine hydrochloride preparations by the transformation to freebase and crack cocaine was carried out. In addition, cocaine and amphetamine preparations as well as adulterated marijuana were smoked in a specially adapted smoke apparatus, which should simulate the smoke behaviour of a consumer. The apparatus was validated for this purpose with non-adulterated marijuana previously. The aim of the present study was the analysis of substances (cutting agents) which passed over into the smoke as well as the detection of pyrolysis properties of the smoked preparations.

2. Materials and Methods

2.1. Materials

2.1.1. Construction of the smoke apparatus

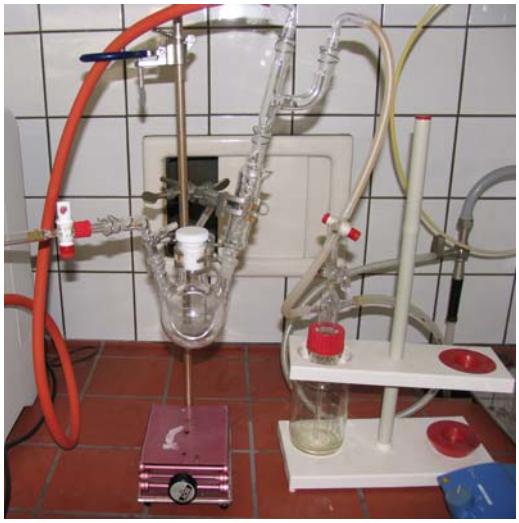

Fig. 1. Construction of the smoke apparatus used for the smoke attempts consisting of a glass frit column (NS 14.5), a silicon sealed thermometer adaptor (NS 14.5), a vacuum thrust (NS 14.5), a 250 ml three-neck round-bottom flask with a Vigreux column (NS 14.5) [or alternatively with a Liebig condenser (NS 14.5)], a two-neck adaptor (NS 14.5), two adaptor with olive, a 500 ml washing bottle and a water jet pump with a vacuum measurement display. For the respective question the apparatus was checked and changed if necessary to achieve optimum results.

2.1.2. Chemicals and reagents

Marijuana samples from seizures in the illicit drug market [sample no.: a) 100; b) 110; c) 150]; tobacco (Natural American Spirit); Rotisol ≥ 99 %; tribenzylamine (TBA) > 99 %; nitrogen 5.0; argon; liquid nitrogen; amphetamine sulphate (a) Merck; b) sample no.: 200; c) sample no.: 210); $C_{20}H_{42}$ (icosane) ≥ 98 %; sodium lye 2M; methyl *tert*-butyl ether 99,5 %; pyridine ≥ 99 %, p.a.; MBTFA; Cocaine samples from seizure of the illicit drug market [a) sample no.: 300; b) sample no.: 310; c) sample no.: 350; d) sample no.: 380]; 10% ammonia solution; $C_{24}H_{50}$ (tetracosane) ≥ 99 %; $CHCl_3$ ≥ 99 %, p.a.; MSHFBA; potassium dihydrogen phosphate (anhydrous); ammonium formate (> 97 %); nitrite ion chromatography standard (1000 g/L); multi elements ion chromatography anion standard solution (fluoride: 3 mg/kg, chloride: 10 mg/kg, bromide: 20 mg/kg, nitrate: 20 mg/kg, sulphate: 20 mg/kg, phosphate: 30 mg/kg); sodium chlorate (≥ 98 %).

2.2. Methods

2.2.1. Analyses of non-smoked and smoked amphetamine sulphate, freebase cocaine and crack samples

Preliminary remarks: Weighing of smoking condensates (substances which passes over into the smoke or precipitated on the glass vessels) was not possible, therefore the relative ratios of the peak areas (GC-PND) of the source preparations (marijuana, amphetamine and cocaine preparations) were compared with those of the preserved smoke condensates (shown in the tables below). The determined relative peak ratios of the amphetamine preparations were always corresponded to the amphetamine base, relative peak ratios of the cocaine preparations to cocaine hydrochloride and the relative peak ratios of marijuana based on the previously achieved amounts of THC.

2.2.1.1. Validation of the smoke apparatus for the suitability in smoking marijuana

400 mg marijuana were crushed and transferred into a glass frit column (Fig. 1.) and slightly pressed onto the ground of the frit with a cotton bud. A vacuum of 940 mbar (pump pressure with closed apparatus) and/or 970 mbar (with slightly open apparatus) was adjusted by the use of the water jet pump. The sample was inflamed with a wooden stick. Smoking procedure was regulated by adjusting the vacuum with the three-way valve - three seconds of ventilation of the smoking apparatus simulated the exhalation, while five seconds of vacuum simulated the inhalation. Cooling of the three-neck round-bottom flask with water or alternatively with ice water was necessary to retain most of the active substances, which passed over into the smoke. For the gas analysis samples, liquid nitrogen was used as cooling agent. After the entire combustion of the applied material the smoking apparatus was left for some minutes to assure the condensing of the smoke completely inside the apparatus. The smoke condensate was transferred into 10 ml roll edge snap bottles or 50 ml Erlenmeyer flask by rinsing the glass vessels with ethanol for several times. Therefore four kind of samples were taken, to check the cooling effects of the round-bottom flask: a) outlet of the glass frit column with thermometer adaptor; b) vacuum piping with the 250 ml three-neck round-bottom flask; c) Vigreux column or Liebig condenser; d) two-neck adaptor and adapter with olive and if necessary, a test from the washing bottle (e). The ethanol solved smoke condensates were put on a 50°C hot plate (according to the smoked material) and ventilated with nitrogen until dryness. As reference non adulterated material tobacco ("Natural American Spirit") was smoked in a similar way. Smoking procedures were carried out 2-3 times (adulterated marijuana, amphetamine, cocaine).

2.2.1.2. Preparation of freebase cocaine according to a lab-internal protocol

3 g of a cocaine hydrochloride preparation were solved in 30 ml tepid water in a 50 ml Erlenmeyer flask. The mixture was treated with an ammonia solution (10%, v/v) until precipitation was finished. The pH of the solution was checked with indicator paper (pH should be > 9). The freebase cocaine was separated via extraction with methyl *tert*-butyl ether in a separatory funnel and afterwards dried under a stream of nitrogen at 50°C for approx. 1 h. The yield was determined by weight.

2.2.1.3. Preparation of crack cocaine according to a lab-internal protocol

3 g of a cocaine hydrochloride preparation and 1.5 g sodium hydrogen carbonate were dissolved in 30 ml water in a 50 ml Erlenmeyer flask. The solution was boiled on a hot plate until no more precipitation occurred (approx. 5 ml of the solution remained in the flask). Afterwards, the precipitate was filtered and washed with 5 ml ice water for several times. The product was dried for 4 h at 50°C and the yield was determined by weight.

2.2.1.4. Smoking procedure of amphetamine sulphate/-preparations in the smoke apparatus

Amphetamine sulphate or amphetamine sulphate preparations were smoked similar as described for freebase cocaine and crack. Therefore 50 mg or 150 mg of amphetamine sulphate or the preparation (according to potency of the sample) were mixed with the tobacco of one cigarette (“Natural American Spirit") and smoked. According to the results of the validation only two kind of samples were taken of the smoke apparatus: a) outlet of the glass frit column with thermometer adaptor and b) remaining part of the smoke apparatus.

2.2.1.5. Smoking procedure of 4-fluoroamphetamine-base

50 µl 4-fluoroamphetamine-base were dropped on the tobacco of one cigarette “Natural American Spirit” and smoked in the smoke apparatus as described for freebase cocaine and crack. Quantification was carried out like in detail described under 2.2.1.8.

2.2.1.6. Smoking of freebase and crack cocaine in the smoke apparatus

50-150 mg freebase cocaine or crack preparations were smoked under a constantly reduced pressure by means of a Bunsen burner in the smoke apparatus. Only one sample was taken for the analysis (complete smoke apparatus).

2.2.1.7. Quantification of THC in adulterated and non-adulterated marijuana samples and the smoke condensates

10 mg tribenzylamine (TBA; ISTD) and 10 ml ethanol (95:5, v/v; ethanol/acetone) were mixed with the dry marijuana smoke condensate or 200 mg of the marijuana sample. The mixture was solved in an ultrasonic bath for 15 min. 1 ml of this solution was filled into a GC-vial and measured by GC-FID (1 µl).

2.2.1.8. Quantification of amphetamine in adulterated and non-adulterated amphetamine sulphate preparations and smoke condensates

100 mg amphetamine or the whole dry amphetamine smoke condensate and 50 mg of $C_{20}H_{42}$ (ISTD) were mixed with 10 ml sodium lye (2M) and 40 ml methyl *tert*-butyl ether in an Erlenmeyer flask. The two phases were incubated for 15 min in an ultrasonic bath. 1 ml of the ether phase was pipetted into a GC-vial and mixed with 100 µl pyridine and 300 µl of N-methyl-bis(trifluoroacetamide) (MBTFA). The vial was closed, mixed by mild shaking and examined with GC-FID (1 µl).

2.2.1.9. Quantification of cocaine in adulterated freebase and crack cocaine preparations and smoke condensates

25 mg of a cocaine preparation or the whole dry smoke condensate and 10 mg $C_{24}H_{50}$ (ISTD) were mixed with 8 ml chloroform. The mixture was treated in an ultrasonic bath for 15 min. 750 µl of the solution were filled in a GC-vial and mixed with 100 µl pyridine and 250 µl N-methyl-N-trimethylsilyl-heptafluorobutyramide (MSHFBA). The mixture was incubated for 10 min at 80°C in a heat bath and measured by GC-FID (1 µl).

2.2.1.10. Analyses and quantification of the adulterants

Analyses were carried out using GC-FID, GC-PND as well as GC-MS. Some additional analyses were carried out by the use of HPLC-TOF-MS.
GC-FID: Adulterants were quantified by single-point calibration. Sample preparation (freebase and crack cocaine, amphetamine) was carried out as described above. Adulterants were quantified in the freebase and crack preparations as well as in the amphetamine preparations.
GC-MS: The dry smoke condensates of the adulterated amphetamine and cocaine preparations were mixed with 1 ml of a pyridine:chloroform solution (2:8, v/v) and derivatized with MBTFA (amphetamine) or MSHFBA (cocaine). The cocaine samples were placed into a heating/thermal bath for 30 min at 80°C. 1 µl of the samples were analysed by GC-MS.
GC-PND: 2 mg of the freebase and crack cocaine preparations, the amphetamine preparations as well as the dry smoke condensates were mixed with 1 ml ethanol and analysed by GC-FID.
HPLC-TOF-MS: Dry smoke condensates of the adulterated amphetamine and cocaine preparations were dissolved in water/acetonitrile (50:50, v/v) and analysed by HPLC-TOF-MS.

2.2.2. Analyses of adulterated marijuana

Analyses of the adulterated marijuana sample were carried out via scanning electron microscopy, light microscopy, X-ray diffraction, ion and gas chromatography and HPLC-TOF-MS.

2.2.2.1. Quantification of anions via ion chromatography

As a standard for the ion chromatography, 1 ml of the multi elements ion chromatography solution was mixed with 100 µl of a nitrite standard solution (g/ml) and 100 µl of an acetate standard solution (g/ml) in 100 ml distilled water.
Analyses of anions were carried out in 10 ml solutions.

a) Rinsing of the marijuana adulterated with fertilizer
b) Smoke condensate of the adulterated marijuana
c) Non adulterated marijuana as reference (sample no.: 100)

Solutions were filtered before each measurement.

2.2.3. Instrumentation

GC-FID: Agilent 6890 GC coupled with a FID. Column HP-1 ultra 25 m, 0.32 mm i.d., 0.17 µm df, carrier gas Nitrogen, injector 300°C
THC: 1.0 ml/min, oven: init 210°C, 3.0 min, rate 6°C/min, to 300°C for 3 min, run time 21 min, split 50:1
Amphetamine: 1.1 ml/min, oven: init 120°C, 3 min, rate 10°C/min, to 300°C for 3 min, run time 21 min, split 50:1
Cocaine: 1.0 ml/min, oven: init 210°C, 3 min, rate 6°C/min, to 300°C for 0 min, run time 18 min, split 50:1

HPLC-TOF-MS: Agilent system LC 1200 Series coupled with Bruker MS microTOF-Q II. Column YMC-Pack ODS-AQ 150 mm, 2 mm i.d., 3 µm df, eluent 30% acetonitrile/70% water containing 0.05% formic acid, 0.2 ml/min, ESI 4500 V (50-1000 amu) SCAN mode

GC-PND: Agilent 6890 coupled with a PND. Column HP-1 ultra 25 m, 0.32 mm i.d., 0.17 µm df, carrier gas Nitrogen, injector 300°C, 1.2 ml/min, oven: init 100°C, 2 min, rate 10°C/min, to 300°C for 6 min, run time 28 min, split 40:1

GC-MS: Agilent 6890 coupled with a MSD 5973. Column HP-5MS 5% Methyl Siloxane 30 m, 250 µm i.d., 0,25 µm df, carrier gas Helium (5.0), 1.0 ml/min, injector 250°C, oven: init 70°C, 2.0 min, rate 20°C/min, to 300°C for 20 or 23 min, run time 35.50 or 36.50 min, split 50:1, EI mode 70 eV, SCAN 40-600

Ion chromatography: 861 Advanced Compact Metrohm. Column Metrosep A supp 4 250 mm, 4 mm i.d, eluent a solution of 1.9 mmol/l sodium carbonate, 1.0 mmol/l sodium hydrogen carbonate and 5 % acetonitrile, temperature 20°C, 1 ml/min

3. Results and Discussion

3.1. Analyses of adulterated amphetamine sulphate preparations

It is well known that amphetamine sulphate could not be smoked, since it pyrolysed at the occurred temperatures during the smoking procedure. In form of the base, amphetamine however, passes over into to the smoke in sufficient amounts and could be easily taken up by the lung of a consumer. But this would affect the respiratory pathways belonging to the strong basicity of the amphetamine base. Therefore it was not converted to its free base, and the aim of the present study was to examine, whether amphetamine sulphate as well as adulterants contained in amphetamine sulphate preparations could be smoked. Besides 4-fluoroamphetamine was tested, since it is often used as an adulterant in amphetamine sulphate preparations. In addition to sugars the most common adulterant is caffeine.

The potencies of amphetamine sulphate and amphetamine sulphate preparations were measured before (amphetamine sulphate 74.7 %; sample no.: 210 10.3 %; sample no.: 200 3.56 %) and after the smoking procedure (0.51 – 18.44 %) via GC-FID. In some of the smoke condensates amphetamine could not be detected (sample no.: 200). Therefore more analyses were carried out via GC-PND, GC-MS and HPLC-TOF-MS, to confirm that amphetamine (at low concentrations), but also caffeine and 4-fluoroamphetamine could be smoked and therefore reached the body of the consumer. Amphetamine, as well as caffeine and 4-fluoroamphetamine could be detected via the mentioned methods.

Quantification of smoke condensates, which may contain 4-fluoroamphetamine, resulted in a potency of 0.046 %, corresponded to 0.069 mg active substance after the smoking of 150 mg of an amphetamine sulphate preparation. As reference material pure 4-fluoroamphetamine (100 %; 52.1 mg) was smoked. 0.82-3.51 mg 4-fluoroamphetamine could be detected in the smoke condensates via GC-FID. Since only few information on 4-fluoroamphetamine exists, toxic effects and the damage potential of this substance for the lung remain uncertain. However, it could be supposed that 4-fluoroamphetamine may cause similar effects as amphetamine and MDMA. Reliable data on the toxic effects of 4-fluoroamphetamine are not available. Also it is not known in which way amphetamine would be smoked by consumers, like it is known for cocaine. In the present study, the amphetamine sulphate or the corresponding preparations were smoked after admixture of tobacco. Other smoking procedures of amphetamine are possible, since recently amphetamine was found in some cocaine preparations.

Quantifications of the adulterants in such amphetamine sulphate preparations were carried out by calculating the relative ratios of the peak areas. Therefore, the measured GC-PND peak areas of the source preparations were compared with those of the condensates (Tab. 1).

Tab. 1. Overview of the adulterated amphetamine preparations and the percentile amount of the adulterants in the smoke condensates.

No.	Drug potency (GC-FID) [%]	Adulterant potency (GC-FID) [%]	Adulterant	Peak area drug source preparation (GC-PND)	Peak area adulterant source preparation (GC-PND)	Peak area smoke condensate drug	Peak area smoke condensate adulterant	Rel. ratio of the peak areas drug/adulterant *not smoked* (GC-PND) [%]	Rel. ratio of the peak areas drug/adulterant *in the smoke* (GC-PND) [%]
Amphetamine									
200	3.56	34.38	Caffeine	12.63	2016	84.99	8959	99.4	99.1
						55.24	6447		99.2
		3.92	4-FA		8.13	84.99	67.04	39.2	44.1
						55.24	46.17		45.5
210	10.3	30.55	Caffeine	45.67	1910	6.59	234.72	97.6	97.2
						31.62	253.44		88.9

The results demonstrated, that it is possible to smoke amphetamine sulphate as well as caffeine and 4-fluoroamphetamine. Besides it shown, that the relative ratios of the peak areas in the source preparations are nearly the same as in the related smoke condensates. Therefore, it could be figured out that not only the drug itself reaches the lung of the consumer, but also the adulterants within the drug preparations. Interactions between the mentioned adulterants and the smoked drug cannot be excluded. According to laboratory experience, 1 g of an average amphetamine sulphate preparation is adulterated with about 0,7 g caffeine, which correspond to a consumption of 7 cups coffee in a typical single dose of amphetamine (50 mg). Hence, increasing of the dependency potential due to compounds related to ephedrine is possible. Withdrawal symptoms like headaches, daze, tiredness, interferences of intellectual and motor abilities and concentration deficit [4] resulted of discontinue after caffeine consumption after longer expositions.

3.2. Analyses of adulterated freebase and crack cocaine preparations

Analogue to amphetamine sulphate, cocaine hydrochloride could not be smoked, since it pyrolysed during the smoking procedure. Therefore, cocaine preparations adulterated with lidocaine, procaine, diltiazem, hydroxyzine, levamisole, caffeine and phenacetin, were converted to freebase as well as crack cocaine samples, analyzed and then smoked in a suitable apparatus. The smoke was condensed and analyzed. As expected, smoking procedure could not be adapted precisely to the smoke behaviour of a consumer, while different smoke conditions resulted in different relative peak area ratios (drug/adulterant) (Tab. 2). Besides, results were also not reproducible. Cocaine could still be detected in all smoke condensates. The active substance amounts of the condensates differ between 1.4 mg (minimum) to 33.9 mg cocaine (maximum) in relation to 100 mg smoked freebase cocaine preparation, with active substance abundance of 55.6 – 67.5 mg cocaine. The active substance amount of the smoked crack preparations differ between 1.0 mg and 27.7 mg in relation to 150 mg or 50 mg of the preparation, with a active substance amount of 36.2 mg or 50.4 mg.
The preparation of freebase and crack cocaine may eliminate sugar and sugar alcohols, but all other examined adulterants were presented in the cocaine samples. Smoke analyses with GC-PND, GC-MS and HPLC-TOF-MS show that adulterants were detected in similar ratios. Phenacetin, lidocaine, procaine and diltiazem showed the best recovery. Even levamisole could be found, but was not quantified as well as procaine. Toxic effects of the detected adulterants on the lung are unclear and topic of further research. Beside the mentioned adulterants, the list of other cutting agents is long. More and even new compounds are expected as adulterants of illicit drugs. Because most examinations in the State Bureau of Criminal

Investigation were done on huge seizures, it can be assumed that drug preparations consumed by the end users are by far more adulterated. The percentile amounts (%) of the adulterants were calculated analogue to the amphetamine preparations (Tab. 2).

Tab. 2. Overview of the adulterated freebase and crack cocaine preparations and the percentile amount of the adulterants in the smoke condensates.

No.	Drug potency [%] (GC-FID)	Adulterant potency [%] (GC-FID)	Adulterant	Peak area drug source preparation (GC-PND)	Peak area adulterant source preparation (GC-PND)	Peak area smoke condensate drug (GC-PND)	Peak area smoke condensate adulterant (GC-PND)	Rel. ratio of the peak areas drug/adulterant *not smoked* (GC-PND) [%]	Rel. ratio of the peak areas drug/adulterant *in the smoke* (GC-PND) [%]
Freebase cocaine									
300	67.5	28.48	Phenacetin	2449	744	3012.0	1993.0	23.3	39.8
						189.3	509.8	23.3	72.9
						652.2	1051.8	23.3	61.7
						352.7	2175.9	23.3	86.1
						532.0	2703.6	23.3	83.6
		6.63	Lidocaine		602	3012.0	1526.8	19.7	33.6
						189.3	464.6	19.7	71.1
						652.2	768.3	19.7	54.1
						352.7	1861.1	19.7	84.1
						532.0	2218.4	19.7	80.7
380	42.9	4.91	Diltiazem	1360	270	644.6	382.3	16.6	37.2
						1368.3	426.4	16.6	23.8
		53.92	Phenacetin		1424	644.6	7804.6	16.6	92.4
						1368.3	9113.5	16.6	86.9
310	55.6	0.21	Caffeine	2020	37	13655.5	402.6	1.8	2.9
						12681.9	368.9	1.8	2.8
		3.07	Diltiazem		159	13655.5	662.2	7.3	4.6
						12681.9	649.0	7.3	4.9
		2.46	Hydroxyzine		106	13655.5	283.3	5.0	2.0
						12681.9	424.5	5.0	3.2
		39.79	Phenacetin		1042	13655.5	9211.4	34.0	40.3
						12681.9	6234.5	34.0	33.0
350	80	/	Procaine	/	/	/	/	/	/
Crack cocaine									
310	24.1	0.6	Caffeine	755	108	241.8	916.2	12,5	79.1
						1463.8	656.5	12,5	31.0
		68.49	Phenacetin		1850	241.8	4985.9	71,0	95.4
						1463.8	4671.8	71,0	76.1
		1.48	Hydroxyzine		57	241.8	52.5	7,0	17.8
						1463.8	104.6	7,0	6.7
		1.25	Diltiazem		84	241.8	128.1	10,0	34.6
						1463.8	218.6	10,0	13.0
350	100.7	/	Procaine	/	/	/	/	/	/

The results demonstrated, that each examined adulterant can be smoked and reaches the lung in higher amounts than the drug itself (e.g. phenacetin is found in 20 fold amount to cocaine). This indicates that the consumer seems to be more affected by the adulterants than by the drug itself. Procaine was not quantified, but analyses with the GC-PND show that it also can be

smoked. Lactose or other sugars could not be detected, demonstrating that it could not be smoked or was eliminated before.

3.3. Analyses of adulterated marijuana

Adulterated marijuana (potency 8.05 %) was analyzed via light (Fig. 2) and scanning electron microscope (Fig. 3).

Fig. 2. Dried marijuana sample. Left: the whole marijuana blossom with some white crystals on it. Right: trichomes of the marijuana blossoms with white crystals.

Therefore, the crystalline white solid on top of the sample as well as a rinsing of the solid was examined. The elemental analysis showed that the main part of the crystalline solid consists of the elements phosphorus and potassium (Fig. 3).

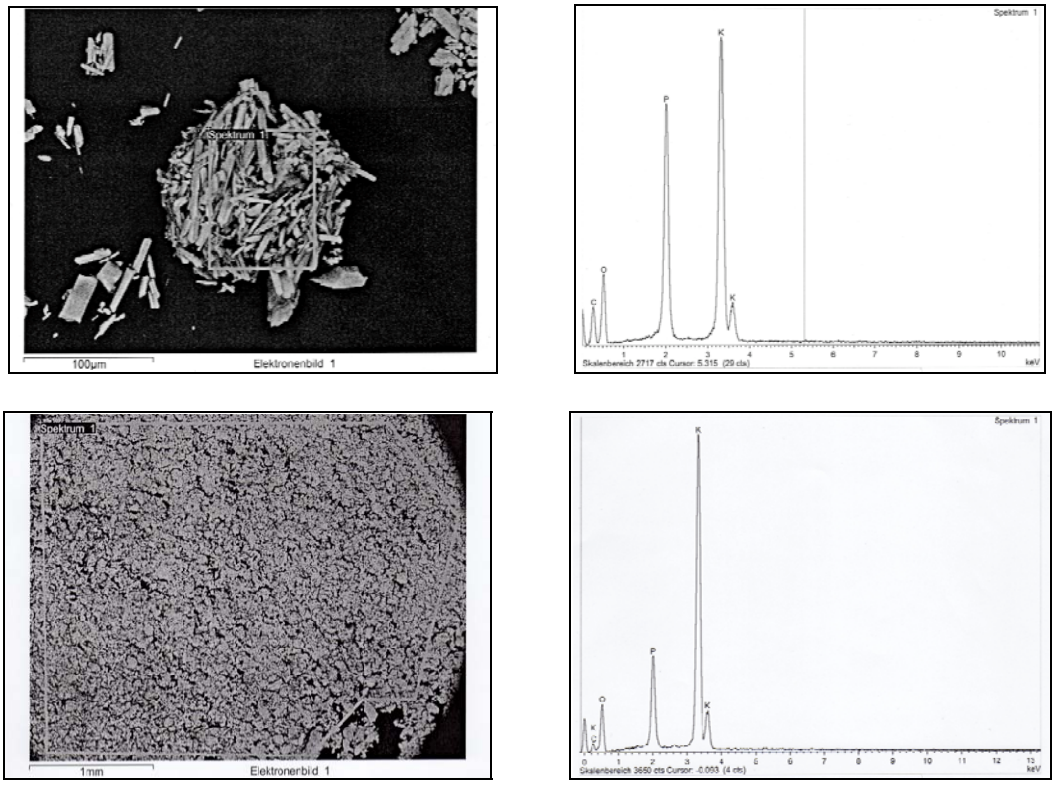

Fig. 3. Analyses via scanning electron microscopy of the white solid of the marijuana (above) and rinsing of the solid (bottom).

Further investigations were carried out by wet chemical analysis and ion chromatography. The analyses confirm the evidence of phosphorus. Furthermore, the presence of nitrate, fluoride, chloride and sulphate was confirmed. These results indicated that the marijuana must have been treated with a potassium-phosphate/-nitrate fertilizer in the time between breeding and sale. Quantifications were carried out via anion chromatography. Thus 160 mg marijuana contained of 14.93 mg phosphate, 8.80 mg nitrate and low amounts of fluoride, chloride and sulphate. Therefore, it could be assumed that the marijuana sample (593 g) was adulterated with 55.33 g phosphate, 32.62 g nitrate and 8.11 g fluoride-, chloride- and sulphate. The amount of the counter ion potassium for nitrate, phosphate and the other ions, was estimated. Belonging to the approval, that for each phosphate ion one potassium ion had to be established to form potassium dihydrogen phosphate, an overall amount of 22.78 g potassium were present. For nitrate 20.57 g and for the other ions 14.66 g of potassium were calculated, resulting in about 27 % fertilizers on the marijuana. In the smoke condensates of the adulterated marijuana lower amounts of the mentioned ions could be detected. Besides, formate or acetate as well as nitrite could be found (Fig. 4).

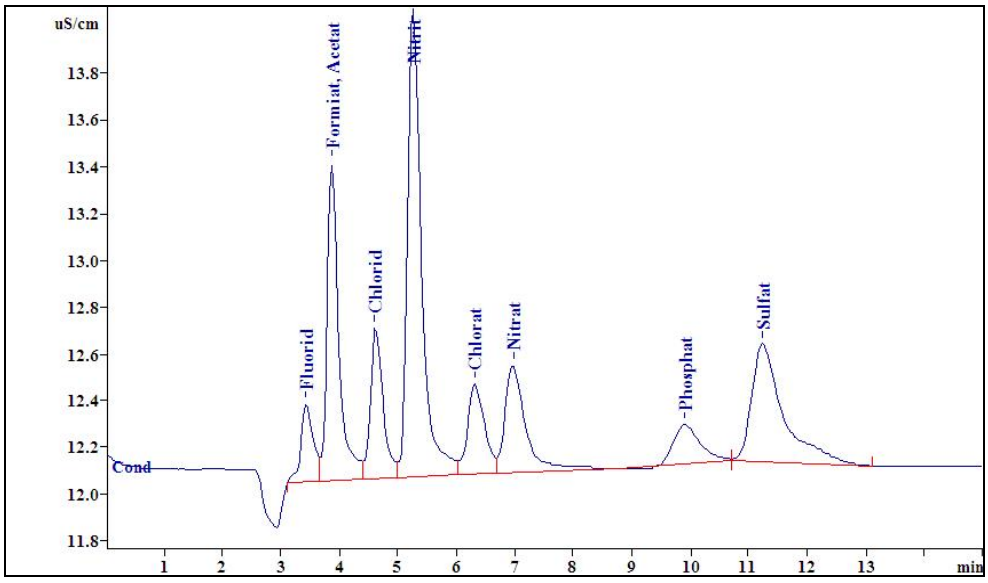

Fig. 4. Ion chromatogram of a marijuana smoke condensate.

Additional analyses of the smoke via Headspace-GC-MS-SPME show also the presence of nitrogen oxide, which seems to be a possible explanation for respiratory effects described by some consumers. Moreover, the adverse effects of nitrite and/or nitrogen oxide last from headaches to acute symptoms like methemoglobinemia and hypotension [5].

For the final assessment of the white solid crystals X-ray diffraction was carried out. Solid crystals as well as a rinsing of the crystals were examined. Potassium dihydrogen phosphate and potassium nitrate were analyzed as the major compounds of the solid, which is a further indication that the marijuana was adulterated with a fertilizer (Fig. 5).

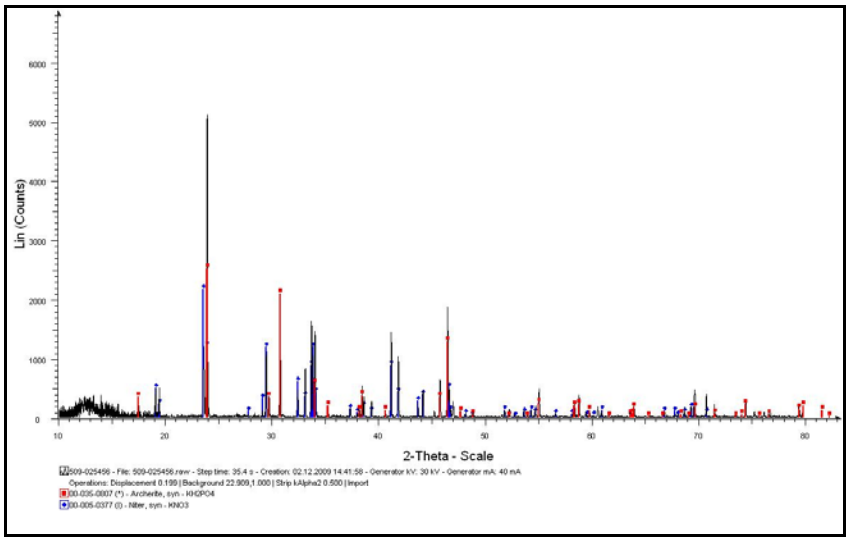

Fig. 5. X-ray spectra of the adulterant (red) and a rinsing of the adulterant (blue).

4. Conclusion

We concluded that the adulterants caffeine, 4-fluoroamphetamine, phenacetin, hydroxyzine, diltiazem, lidocaine, levamisole and procaine contained in amphetamine or cocaine preparations as well as fertilizers (on marijuana samples – via degradation) can be smoked, since they were found in the smoke condensates after the smoking procedure with the described smoke apparatus. The toxic effects to the lung, caused by that substances are so far unclear.

5. References

[1] Brunt MT, Rigter S, Hoek J, Vogels N, van Dijk P, Niesink MJR. An analysis of cocaine powder in the Netherlands: content and health hazards due to adulterants. Addiction 2009;104:798-805.

[2] Busse PF, Fiedler MG, Leichtle A, Hentschel H, Stumvoll M. Lead Poisoning Due to Adulterated Marijuana in Leipzig. Dtsch Arztebl Int 2008;105:757–62

[3] http://hanfverband.de/index.php/themen/konsumentenhilfe/1050-streckmittel-in-marihuana-wie-man-sie-erkennt-und-welche-risiken-von-ihnen-ausgehen. Deutscher Hanf Verband (DHV).

[4] Julien RM. Drogen und Psychopharmaka. Spektrum Akad. Verl. Heidelberg, Berlin, Oxford 1997;175-176

[5] Tran CD, Brazeau AD, Nickerson AP, Fung LF. Effects of repeated in vivo inhalant nitrite exposure on gene expression in mouse liver and lungs. Elsevier Nitric Oxide 2006;14:279-289.

---

[i] The internet reference that claimed these findings still has to be verified – maybe it reports also on a misunderstanding – about “Brix” is reported it would be used “solely for the cutting of marijuana”. In original language: „Brix wird in Australien und den USA hergestellt und dient **ausschließlich dem Strecken von Marihuana**. Es ist eine Flüssigkeit, die aus Zucker, Hormonen und flüssigem Kunststoff besteht. Zum Strecken werden die Marihuanablüten (Buds) vor dem Trocknen in Brix getaucht oder mit ihm besprüht.“ Quelle: http://hanfverband.de/index.php/themen/konsumentenhilfe/1050-streckmittel-in-marihuana-wie-man-sie-erkennt-und-welche-risiken-von-ihnen-ausgehen