

19th IAFS WORLD MEETING
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ORAL SESSION

Session 15.4

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LEGAL IMPLICATIONS OF AND CURRENT ANALYSIS STRATEGIES FOR CANNABIMIMETIC AMINOALKYLINDOLES IN HERBAL MIXTURES - FOLLOW-UP OF THE "SPICE" PHENOMENON

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Abstract: Starting from 2004 herbal mixtures like 'Spice' were sold in many European countries mainly via internet. Although declared as incense, they are smoked by the consumers as a Cannabis substitute. In 2008 the popularity of these herbal drugs increased dramatically in Germany and other countries as they were widely sold by head- and smart shops to consumers without age restriction. Drug users reported intense cannabis-like effects after smoking and denied detectability by commonly used drug tests. Although some of the indicated herbal ingredients are potentially bioactive, the suspicion was raised that synthetic cannabimimetic adulterants could be responsible for the reported psychotropic effects. After the identification of the first two synthetic compounds of this kind in 'Spice' and related products in late 2009, the non-classic cannabinoid CP47,497-C8-homolog and the cannabimimetic aminoalkylindole JWH-018, and their subsequent submission to the controlled substance acts of many countries, an ever increasing number of new cannabimimetic designer drugs, mainly aminoalkylindoles, have been identified in follow-up "herbal" products (JWH-250, JWH-081, JWH-122, JWH-210, AM-694, RCS-4 and many more) in 2010 and 2011. The controlled substance acts often lag behind this accelerating new drug phenomenon and the forensic laboratories sometimes can only identify new surfacing substances by chemical structure-elucidating, cost-intensive and not commonly available analytical techniques like NMR and HR-MS. In this presentation, two different approaches of the prosecution of drug crimes related to the new cannabimimetic designer drugs in herbal mixtures will be discussed and counterbalanced - the violation of the medicinal products act by illicit trade of precarious pharmaceutical preparations and the amendment of the controlled substance act with respect to the possibility of submitting complete classes of structurally related substances (in advance of their actual appearance on the drug market). Furthermore, strategies will be presented, how large seizures of these new types of illicit drug products can be processed in the forensic laboratories. New rapid screening procedures for cannabimimetic aminoalkylindoles with ion mobility spectrometry are presented as well as cost-effective high-throughput techniques for these cannabimimetics like thin layer chromatography coupled to desorption-electrospray-ionization-mass spectrometry (TLC-DESI-MS) will be presented and their suitability for forensic casework demonstrated by examples of currently seized and analyzed samples of new herbal products.

Keywords: Synthetic Cannabinoids; "Spice" Products; Designer Drugs; DESI-MS; Ion Mobility Spectrometry

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A ROADSIDE SURVEY OF ALCOHOL, DRUGS AND BENZODIAZEPINES USE AMONG DRIVERS IN PORTUGAL

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Introduction: Driving performance is easily impaired as a consequence of alcohol, drugs and medicines use. Although alcohol is the most frequently detected compound among accident drivers, illicit drugs and psychoactive medicines have also gained considerable attention during the last years. Most epidemiological studies on illicit drugs and medicines among drivers are difficult to compare due to the lack of standardized protocols (e.g. selection of subjects, biological matrix, diversity of compounds included in the analytical program and their cut-off limits). An important project in this field is the European Union project DRUID (Driving Under the Influence of Drugs, Alcohol and Medicines). The participation of the Portuguese National Institute of Legal Medicine in this study allowed, for the first time, to obtain data on the prevalence of alcohol, drugs and medicines among drivers in Portugal.

Materials and Methods: To ensure comparability between results from different countries, uniform design and protocols for the roadside survey were used. A list of core substances as well as analytical cut-off values for oral fluid and blood, were adopted by all countries participants in this study. In Portugal 3965 samples of oral fluid were analyzed by LC-MS/MS for screening and quantification of 26 substances, 23 of which were common to all participant countries.

Results: The presence of at least one psychoactive substance was detected in almost 10% of drivers. Alcohol alone was detected in 4.93% of the cases. Benzodiazepines and THC with a prevalence of 2.73% and 1.38% respectively, were the substances most prevalent after alcohol. The prevalence of cases with alcohol-drugs combination (0.42%) was approximately twice of those with multiple drugs (0.23%). THC was present in more than half of the cases with alcohol-drug combination, while cocaine or its metabolite were present in all cases of multiple drugs involving illicit drugs. In all illicit opiates positive cases, a direct marker of recent use of heroin, 6-acetylmorphine, was detected. Methadone was detected in 80% of the positive cases for medicinal opioids. Benzodiazepines detected with the highest prevalence were nordiazepam (59%) and alprazolam (26%). The prevalence of alcohol in male (6.21%) was more than two times higher than among female drivers (2.59%). In both groups, the age group 18-24 showed a higher prevalence: 9.76% in male and 8.00% in female drivers. The age groups 18-24 and 25-34 are those with higher prevalence of THC. Benzodiazepines use was significantly higher among females (4.75%) than among males (1.68%). Drivers in the age group 50+ showed a higher prevalence of benzodiazepines (4.58%). Prevalence of alcohol-drugs and multiple drugs is much higher among male (0.64% and 0.32% respectively), than in female drivers (0.01% and 0.08%). With the exception of medicinal opioids, all substance groups showed a higher prevalence at night-time (22:00 to 3:59), being alcohol (9.00%), cocaine (0.37%), THC (3.25%) and illicit opiates (0.37%) more prevalent on weekend nights and benzodiazepines (4.58%), alcohol-drugs (0.51%) and multiple drugs (0.53%), on week nights.

Conclusions: The evidence of this survey, based on a random sampling mechanism that allocates equal probabilities for selection of non-drinking or drinking drivers, would be different if data had been based on the results of the usual enforcement actions. These actions are usually focused on road sites and time periods, whose probability of selection drinking drivers are higher than non-drinking. For this reason the information provided by this study is of particular relevance for planning drug-driving prevention and enforcement activities in the future.

Keywords: Roadside Survey; Drivers; Alcohol; Drugs; Benzodiazepines

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EMERGING DRUG THREATS - SYNTHETIC CANNABINOIDS, CANNABIMIMETICS AND SUBSTITUTED CATHINONE DESIGNER DRUGS

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Introduction: After attending this lecture, attendees will have been presented with an overview of emerging drug threats confronting the United States and other nations around the world. Topics covered will include synthetic cannabinoids, cannabimimetics, and substituted cathinones. Such materials are currently sold in smoke shops, convenience stores, and on the Internet as "legal" products, not for human consumption. However, several of the compounds in the products are now controlled substances, and those that are not specifically controlled may still be subject to treatment as controlled substance analogues under United States law. The strategy to control these substances at the state and federal level in the United States will be discussed.

Comments: The forensic analysis of such compounds may pose challenges due to the lack of certified reference materials and the requirement to characterize unknowns or synthesize and authenticate reference standards. Also challenging is the nomenclature of these compounds with respect to their IUPAC names, specific stereochemistry, and the way they are identified in controlling statutes. Analytical methodologies utilizing instruments available in most forensic laboratories and characterization strategies via advanced instrumental techniques will be discussed. The "designer" nature of these drug compounds and the challenges associated with investigating, analyzing, and prosecuting cases will be discussed. Their marketing names such as "Spice," "K2," and "Bath Salts," will be addressed. Also discussed will be Internet reports from those allegedly experimenting with the use of these compounds as well as Internet discussion that a series of slightly altered additional cannabinoids, cannabimimetics, and substituted cathinones are already in the pipeline to take the place of the compounds that have been, or are to be controlled. Such discussions forecast the ongoing nature of these emerging drug threats.

Keywords: Emerging Drug Threats; Designer Drugs; Cannabinoids; Cannabimimetics; Substituted Cathinones

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FORENSIC ASPECTS IN TEARGAS TOXICITY "A THOUGHT OUT OF THE BOX"

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Introduction: Teargas is a non-specific term for any chemical used to cause temporary incapacitation through irritation of the eyes and/or the respiratory system. This study is not only concerned with the traditional analysis of tearing materials in biological samples but also of the products of thermal decomposition when the solid content of the grenades converted to gas "smoke" form. The thermal composition forms about 50%-70% of the teargas grenade volume. Potassium chlorate/perchlorate and nitrocellulose commonly used in teargas devices and are classified as explosive materials. This study attempts to relate the analyses of post-explosion chemicals and teargas components.

Materials and Methods: From each of three persons said to be exposed to teargas one blood sample was collected after exposure. CS "o-Chlorobenzylidene Malononitrile" a crimator agent and its metabolites were extracted by liquid-liquid extraction method. Extracts were concentrated and analyzed using gas chromatography with electron impact mass spectrometry (GC/EI-MS). Hp-5 column (30.0 x 25 cm x 0.25 µm) with carrier He gas was used at a flow rate of 0.8 ml/min. Carboxyhemoglobin and cyanoheemoglobin are two of the toxic compounds formed after exposure to teargas. Ultraviolet spectrophotometry was used to detect carboxyhemoglobin. Detection of Cyanide was carried out by blood distillation followed by colorimetric test of ferrocyanide complex formation (Prussian blue color). Experimentally three rats were exposed to the combustion of the thermal composition in a closed area. A blood sample was collected from each rat separately after exposure. The thermal decomposition products perchlorate, chlorate, chloride and nitrite were extracted in the blood serum by centrifuge. The serum was deproteinized using acetonitrile deproteinization procedure. The deproteinized extract was concentrated and analyzed using ion chromatography with a conductivity detector (IC-CD). Ionpac AS 19 column (4 x 250 mm) with eluent 10-40 mmol KOH at a flow rate of 1 ml/min.

Results: CS "o-Chlorobenzylidene Malononitrile" and its metabolite 2-Chlorobenzaldehyde were detected in the blood sample of one person. Carboxyhemoglobin was detected in another person's blood sample, while cyanoheemoglobin was not detected in any of the three analyzed human blood samples. Thermal decomposition products were not detected in the blood of exposed persons. As for samples collected from rats; perchlorates, chlorates, chloride and nitrites were detected by ion chromatography-conductivity detector in addition to the anions found in normal blood IC analysis.

Conclusions: Analytical toxicologists and forensic chemists are interested in detecting Carboxyhemoglobin, cyanoheemoglobin and o-Chlorobenzylidene Malononitrile metabolites in biological samples. The present study stresses the importance of detecting the thermal decomposition inorganic products, since they are known to form methemoglobin causing lack of oxygen which when severe may lead to death.

Keywords: Teargas Toxicity; Methemoglobinemia; CS Teargas; O-Chlorobenzylidene Malononitrile

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ESTIMATING COCAINE CONSUMPTION IN THE BRAZILIAN FEDERAL DISTRICT BY SEWAGE ANALYSIS: QUANTOX PROJECT

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Introduction: Estimating the amount of illicit drugs used by a certain population is one of the main challenges to forensic scientists working with law enforcement. The indicators normally used to follow up and evaluate the results of the police efforts are usually "out of perspective" and not reliable to estimate the total amount of drugs that really reaches the illicit market. An alternative to the epidemiological tools is the utilization of sewage epidemiology to measure concentrations of illicit drugs and their metabolites to provide objective, quantitative, and near real-time profiles of illicit drug consumption as well as to estimate and compare consumption patterns.

Materials and Methods: This work was carried out in the Brazilian Federal District (FD). This region has relatively high percentage (> 93%) of wastewater collection and treatment. The raw sewage samples were collected from six selected WTP, namely Melchior, Asa-Sul, Samambaia, Asa-Norte, Paranoá, and Riacho-Fundo, serving an equivalent population of approximately 1.5 million inhabitants and were collected in March and June 2010. The raw sewage samples were filtered, the pH was adjusted and the solid-phase extraction of cocaine (COC) and benzoylecgonine (BE) was carried out using HLB Oasis cartridges. Analytes were recovered with methanol and the eluates evaporated to dryness with N₂ flow. The analytes were diluted to 1.0 mL in a 0.1% formic acid solution in water:methanol, 90:10 (v/v). The LC-MS-MS was performed in a QqQ mass spectrometer with ESI source in MRM mode, measuring the fragmentation products of ions [M+H]⁺ for COC and BE. Quantification was performed using, at least, 6-point analytical curves and recovery tests showed percentages for both compounds between 95 and 105%.

Results: Among the WTP studied, samples from Samambaia showed higher concentrations (from 3866 to 2477 ng/L of BE and 805 to 579 ng/L of COC) and doses per inhabitants (more than 13 doses/year/inhabitant). The Paranoá and Asa-Norte WTP also showed relatively high consumption (5 and 6 doses/year/inhab., respectively), especially when compared to Asa-Sul, Melchior and Riacho-Fundo WTP (both 3 doses/year/inhab.). The extrapolation to the whole FD population points out to an annual consumption reaching 1.0 ton of free base cocaine, or 1.1 tons of cocaine hydrochloride (100% of purity). The work also addresses the influence of the cocaine presentation form (free base or hydrochloride) and the integration with chemical profiling results in a more realistic estimate, mainly concerning the viewpoints of forensics and law enforcement.

Discussion and Conclusions: Collaborative work involving a team of environmental and analytical chemists guided by a forensic approach broadens the possibility of this type of work, as well as allowing a more comprehensive discussion, not only about illicit drugs but also about other emerging contaminants. From the total estimated consumption of 1.0 ton of free base cocaine in FD, the sampling strategy used in this research provided an additional means of detecting areas with higher consumption in the region covered by the sewage network. As the annual cocaine seizures conducted by Federal Police in the FD are around 450 kg (approximately 30% of the total estimated by this work). Seizures of street samples, which are conducted by Brazilian FD state or military police, are not considered, since no chemical profile data are available yet to establish a common basis for comparison. The importance of the data obtained using sewage epidemiology in forensic, law enforcement, health and public education initiatives led the authors of this paper to propose a broader project called Quantification of Toxic Analytes (QuAnTox) to determine the quantities of cocaine, key metabolites and other illicit drugs in the Federal District, also addressing issues of seasonality, including all WTP and collaborating with a discussion about the increasing tendency observed for the use of smoked crack cocaine.

Keywords: Cocaine; Sewage; Estimate; Illicit Drug; Brasília; Quantox

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NEW SYNTHETIC PSYCHOTROPIC DRUGS - ONE STEP AHEAD OF THE LAW

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Abstract: Since 2008, Cyprus has seen a large number of new synthetic psychotropic drugs on the market, namely synthetic cannabinoids and cathinones sold as herbal air fresheners and bath salts. Large classes of legal compounds have been created by making minor chemical modifications to existing controlled drug molecules. Analysis and identification of these has proved challenging to the forensic drug laboratory due to the unknown nature of the active ingredient, the lack of reference standards for the majority of these compounds and their continuously changing composition. In 2010, the synthetic cannabinoids JWH- 018, JWH- 073, HU-210 and CP 47,497 were placed under control as Class B drugs in the Cyprus Drug Legislation. This was followed by the synthetic cathinones, methylone, mephedrone, MDVP, and methedrone. Examples of these compounds together with their analysis is given. The recent trends in the production of new synthetic drugs has resulted in the production of over 40 new drugs in 2010 according to the EMCDDA. In order to avoid always being one step behind the producers and dealers of these drugs, a generic legislation for synthetic cannabinoids, cathinones and naphyrone, piperazines and phenethylamines was passed in Cyprus in 2011 based on their chemical structure. This legislation covers the majority of drugs in these classes which have been prepared to date and those which can foreseeable be prepared in the future and which may be subject to abuse eg 86 synthetic cannabinoids. Examples of the legislation and the compounds it covers is given. Whereas this legislation goes a long way to blocking the production of the majority of these possible new drugs, it appears that there are no limits to the ingenuity of the drug producers, as recently, products have appeared with unpredicted modifications to existing structures eg by replacement of the alkyl sidechain in the cannabimimetic naphthoylindoles with an alkylhalide. It appears that the drug producers will always be one step ahead of the legislation!!!

Keywords: New Synthetic Drugs; Cannabinoids; Cathinones; Legislation

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DEMONSTRATION CONTROL AGENTS; EVALUATION OF 64 CASES AFTER MASSIVE USE OF THESE AGENTS IN ISTANBUL

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Abstract: An uncontrolled use of demonstration control agents has recently been common practice in Turkey. Several killings and severe injuries, including skull fractures resulting from a close range impact of gas canisters, and a few deaths caused by after effects of the agents occurred during the last 10 years. One of the first occasions of massive use of these agents have taken place during the demonstrations against a meeting of NAC, NATO in 2004 . Sixty four of these cases were evaluated, and treated by Human Rights Foundation of Turkey (HRFT). The files of these 64 cases have been reviewed retrospectively and were classified regarding age, gender, physical and psychological findings as well as other injuries, and this study has been carried out to reveal the short and long term after effects of demonstration control agents mainly Oleasin Capsicum(OC) The applicants were received 1 to 9 days after the tear gas attack. Among 64 cases , 48 were male and 16 were female. Their ages were between 15- 45 with a mean age of 24,9. Maximum referral was 35 applications on the day of the gas attacks. The latest application was 9 days after the attack . Complaints and physical findings due to the tear gas chemicals were highest during the first 3 days. No physical finding were observed with 6 cases who applied during the 8th and 9th days. Demonstration control agents have been widely used recently, and announced to be safe with only short term effects to resolve in 24 hours. However, persisting physical findings for at least 3 days should be considered seriously. The safety and effects of tear gas chemicals known as demonstration control agents were discussed, based on our findings and existing references.

Keywords: Demonstration Control Agents; Gas Bomb; Tear Gas; Pepper Gas; Gas Canister; Toxic Injury