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Early detection of emerging street drugs by near infrared spectroscopy and chemometrics

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ABSTRACT

Near-infrared spectroscopy (NIRs) is spreading as the tool of choice for fast and non-destructive analysis and detection of different compounds in complex matrices. This paper investigated the feasibility of using near infrared (NIR) spectroscopy coupled to chemometrics calibration to detect new psychoactive substances in street samples. The capabilities of this approach in forensic chemistry were assessed in the determination of new molecules appeared in the illicit market and often claimed to contain "non-illegal" compounds, although exhibiting important psychoactive effects. The study focused on synthetic molecules belonging to the classes of synthetic cannabinoids and phenethylamines. The approach was validated comparing results with officials methods and has been successfully applied for "in site" determination of illicit drugs in confiscated real samples, in cooperation with the Scientific Investigation Department (Carabinieri-RIS) of Rome. The achieved results allow to consider NIR spectroscopy analysis followed by chemometrics as a fast, cost-effective and useful tool for the preliminary determination of new psychoactive substances in forensic science.

1. Introduction

New psychoactive substances (NPS), are a large group of synthetic molecules frequently found in the street market as drugs of abuse. Typical examples are synthetic cannabinoids, cathinones, piperazines, and tryptamines. In addition, new drugs are currently proposed, like molecules derivatives of phenethylamines [1] and most of them are not yet completely controlled by international drug conventions, and may pose a public health threat. In particular, the risk is strictly related to the difficulty of predicting the actual consumed dose, due to variability of active ingredients concentration in consumed products, and as opposed to those claimed by the manufacturer. In addition, the difficulty of predicting the actual pharmacological and toxicological effects related to the simultaneous consumption of different psychoactive ingredients contained in single products, requires a rapid screening and identification of these materials.

Recently, a class of "2C" designer drugs, dimethoxyphenyl-N-[(2-methoxyphenyl) methyl]ethanamine) derivatives have become easily obtainable over the internet, particularly 2-(4-iodo-2,5-dimethoxyphenyl)-N-[(2-methoxyphenyl)methyl]ethanamine (25I-NBOMe). Blotter papers containing 25I-NBOMe appeared on the designer drug market in 2011 [2] sold under various names including 25I, INB-MeO, N-bomb, Smiles, Solaris and Cimbi-5. These N-benzyl phenylethylamine derivatives are potent serotonin 5-HT2A receptor agonists [3–5].

Investigation of these (often not illegal) substances by official methods of analysis is usually performed by applying immunoassays [6], gas chromatography (GC) [7,8], capillary electrophoresis (CE) [9,10] or liquid chromatography (LC) [11–14].

Nowadays it is becoming always more important to develop fast, reproducible and easy-to-use preliminary methods to allow the "on street" early detection to decide the following official analysis in forensic laboratories.

In addition, it should be very useful the possibility to have techniques able to give suggestions on the class of molecules when a new drug is found on the market.

Near-infrared reflectance spectroscopy (NIRs) proved to be fast and precise to identify and quantify substances of abuse without destroying the samples [15].

In this work, NIR spectroscopy combined with chemometrics was tested to be proposed as a useful tool to easily and early detect new drug molecules in real street samples. In addition, results demonstrated that NIRs application, supported by chemometrics, could in addition predict the class of molecule of new drugs. Qualitative data was consequently the main focus of this approach.

To this end, standard molecules was analyzed as such and in simulated matrices, to check the matrix influence on the

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spectroscopic signal and to obtain referring scores plots. Validation tests were performed on real confiscated samples, in parallel analyzed by GC–MS.

2. Materials and methods

2.1. Samples

Standard molecules were purchased from LGC Standards (Italian customer – Milano) or kindly provided by Carabinieri RIS (Scientific Investigation Department).

Drug samples in real matrices (either containing illegal known substances or new molecules) were obtained from samples confiscated by Carabinieri as herbal spices and blotter papers. The complete list with related details is reported in Table 1.

2.2. Sample preparation

No sample preparation was necessary for NIRs measurements, as either the standards or the real samples were directly measured.

For the parallel GC–MS analysis, standard and real samples were extracted from the matrices following the validated internal procedure and then analyzed.

Simulated blotter paper or herbal spices were soaked in consecutive aliquots of 0.5 ml of methanol for 6 h and the filtered supernatant was introduced via an auto injector using an injection volume of 10 ul. Sample recoveries were determined by comparing the peak area of the analytes in the extracted samples with the peak area of the corresponding unextracted analytical standards.

2.3. GC–MS parameters

GC–MS analysis were performed using a gas chromatography system coupled to a mass selective detector manufactured by Perkin Elmer (Waltham, MA). The blotter paper extracts were injected automatically in splitless mode. Chromatographic separation was carried out on an HP-5MS capillary column (30 m × 0.25 mm × 0.25 mm) and helium at a constant flow rate of 1 ml/min was used as the carrier gas. The initial column temperature (75 °C) was maintained for 1 min, then increased linearly at a rate of 25 °C/min to 280 °C, and finally maintained for 2 min. The GC injector and the transfer line were maintained at 280 °C. The spectrometer was operated in electron impact mode (EI). The temperatures of the ion source and quadrupole were 200 °C and 100 °C, respectively. Ionization energy was set at 70 eV and positive ions were analyzed. Acquisition was carried out in scan mode from 29 to 450 amu.

Separation and detection of the methanol extracts of herbal spices were performed in split mode (60:1). GC conditions were as follows: the oven temperature was initially set at 80 °C for 5 min, increased to 290 °C with a ramp of 10 °C min and then held at 290 °C for 15 min. The temperatures of the GC inlet and GC–MS transfer line were kept at 250 °C and 290 °C; the ion source was operated at 200 °C with a temperature of quadrupole of 150 °C. The mass spectrometer was operated in scan mode with a mass range of 44–350 amu. Helium was used as the carrier gas at a constant flow rate of 1.0 mL min and a volume of 1 μL was injected.

2.4. NIR measurements

The NIR spectra were collected in in reflectance mode, through the use of an integrating sphere (Thermo Scientific Inc., Madison, WI), by Nicolet 6700 FT-NIR instrument (Thermo Scientific Inc., Madison, WI), equipped with a tungsten-halogen source and an InGaAs detector. The signals were recorded between 10,000 and 4000 cm^{-1}, collecting 82 scans at a nominal resolution of 4 cm^{-1}.

Spectrometer diagnostics and acquisition of the spectroscopic data were carried by Omnicare Suite software (Thermo Fisher Scientific Inc., Waltham, MA) as ASCII files, which were then imported into V-PARVUS 2009 package [16].

Table 1
List of synthetic cannabinoids and phenethylamines considered

Sample	*Substance name*	*Abbreviation*	*Class*	*Structure*
Standard	1-pentyl-3-(1-naphthoyl)indole	*JWH-018*	Synthetic cannabinoid	Indole
Standard	1-pentyl-3-(1 (4methyl)naphthoyl)indol)	*JWH-122*	Synthetic cannabinoid	Indole
Standard	1-pentyl-3-(2 methoxyphenylacetyl)indole	*JWH-250*	Synthetic cannabinoid	Indole
Standard	(1- butyl- 1H- indol- 3- yl)- 1 naphthalenyl- methanone	*JWH-073*	Synthetic cannabinoid	Indole
Standard	(1-pentyl-3-(4-methoxy-1 naphthoyl)indole	*JWH-081*	Synthetic cannabinoid	Indole
Standard	N-(adamantan-1-yl)-1-pentyl-1H-indazole-3-carboxamide	*AKB48*	Synthetic cannabinoid	Indazole
Standard	2-(2,5-Dimethoxy-4-propylphenyl)ethanamine	*2C-P*	Phenethylamine	2C's
Standard	2-(4-chloro-2,5-dimethoxyphenyl)-N-[(2 methoxyphenyl) methyl]ethanamine	*25-C-NBOMe*	Phenethylamine	NBOMe
Standard	4-iodo-2,5-dimethoxy-N-(2-methoxybenzyl) phenethylamine	*25-I-NBOMe*	Phenethylamine	NBOMe

Sample	*Seizured name*	*Identified molecules*	*Class*	*Matrix*
Confiscated samples	*CREAM*	*JWH-250*	Synthetic cannabinoid	*Herbal spice*
Confiscated samples	*DREAM*	*JWH-122*	Synthetic cannabinoid	*Herbal spice*
Confiscated samples	*ORIG D*	*JWH-073*	Synthetic cannabinoid	*Herbal spice*
Confiscated samples	*N-JOY*	*JWH-018*	Synthetic cannabinoid	*Herbal spice*
Confiscated samples	*BONZAI*	*JWH-081*	Synthetic cannabinoid	*Herbal spice*
Confiscated samples	*SPACE ART*	*JWH-018*	Synthetic cannabinoid	*Herbal spice*
Confiscated samples	*YOUCATAN*	*JWH-018*	Synthetic cannabinoid	*Herbal spice*
Confiscated samples	*KING B*	*JWH-073*	Synthetic cannabinoid	*Herbal spice*
Confiscated samples	*MDR 44*	*2C-P*	Phenethylamine	*Blotter paper*
Confiscated samples	*MDR 23*	*25-I-NBOMe*	Phenethylamine	*Blotter paper*
Confiscated samples	*MDR 38*	*25-I-NBOMe*	Phenethylamine	*Blotter paper*
Confiscated samples	*MDR 46*	*25-I-NBOMe*	Phenethylamine	*Blotter paper*
Confiscated samples	*MDR59*	*25-C-NBOMe*	Phenethylamine	*Blotter paper*