Rapid detection of NBOME's and other NPS on blotter papers by direct ATR-FTIR spectrometry

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A B S T R A C T

Blotter paper is among the most common forms of consumption of new psychotropic substances (NPS), formerly referred as designer drugs. In many cases, users are misled to believe they are taking LSD when, in fact, they are taking newer and less known drugs like the NBOMEs or other substituted phenethylamines. We report our findings in quick testing of blotter papers for illicit substances like NBOMEs and other NPS by taking ATR-FTIR spectra directly from blotters seized on the streets, without any sample preparation. Both sides (front and back) of each blotter were tested. Collected data were analyzed by single- and multi-component spectral matching and submitted to chemometric discriminant analysis. Our results showed that, on 66.7% of the cases analyzed, seized blotters contained one or more types of NBOMEs, confirming the growing presence of this novel substances on the market. Matching IR signals were detected on both or just one side of the blotters and showed variable strength. Although no quantitative analysis was made, detection of these substances by the proposed approach serves as indication of variable and possibly higher dosages per blotter when compared to LSD, which showed to be below the detection limit of the applied method. Blotters containing a mescaline-like compound, later confirmed by GC–MS and LC–MS to be MAL (methallylescaline), a substance very similar to mescaline, were detected among the samples tested. Validity of direct ATR-FTIR testing was confirmed by checking the obtained results against independent GC–MS or LC–MS results for the same cases/samples.

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1. Introduction

In recent years, spreading of new, unregulated substances of abuse, referred generally as NPS, also known as novel designer drugs or legal highs (an allusion to the deceptive legal status of such substances on most countries), has become an issue regarding public health in many parts of the world, demanding constant improvements both on the available knowledge pertaining to the chemistry, pharmacology and toxicology of such substances and on their legal regulation as well [1,2]. Among those substances, which include a growing number of substituted phenethylamines, the NBOME series, a generic denomination for phenethylamines presenting a 2-methoxybenzyl group replacing a hydrogen on the amine, have been attracting attention from medical and legal authorities, due to its association with several intoxication cases and even deaths [3–6], causing it to be outlawed in various countries, including Brazil [7,8].

Like LSD, NBOMEs produce hallucinogenic effects acting as partial or full agonists to serotonin $5 - HT_{2A}$ receptors [9], but presenting increased affinity and selectivity [10]. Its undesirable effects, however, include tachycardia, hypertension, agitation, confusion, pupil dilation, aggressiveness, seizures and other effects [11–14], making it much more dangerous and potentially fatal than LSD.

Lower cost, higher availability and the fact that NBOMEs are still considered legal in many countries seem to be causing increased use of such substances and even encouraging commerce of NBOMEs as counterfeit LSD. Recent reports showed that blotters containing NBOMEs were sold in Spain, Austria and possibly other countries as if they contained LSD [15–17], exposing LSD-accustomed users to unexpected dangers.

Forensic analysis of blotters is normally conducted by GC–MS or LC–MS and require sample preparation which include extraction of

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the analytes by soaking blotters on organic solvents, followed by filtration and/or dilution prior to injection, as described by [18], procedures which are both time consuming and sample-destructive. In this work we report our attempts to rapidly detect NBOMEs and other NPS by taking ATR-FTIR spectra directly from the blotters, with no sample preparation. Analysis of the spectra obtained from both faces of each blotter was carried out considering three different levels: single spectrum database comparison, multi-component database comparison (deconvolution) and discriminant analysis (chemometrics). Aside from a faint indentation mark on each side, produced by the ATR vise accessory, samples were undamaged and preserved for further testing.

2. Materials and methods

2.1. Samples

A total of 77 blotter papers decorated with various artwork patterns were taken randomly as samples from 27 street apprehensions conducted by local police forces on the state of Minas Gerais, Brazil, during 2014. Multiple blotters, presenting the same artwork or not, were taken from the same apprehension when possible and tested individually. Spectra of each single blotter were collected once at the back side, which normally presented no artwork, and once at the front side, defined as where the main artwork was located.

2.2. Instrumentation

ATR-FTIR spectra of blotters were taken using a Nicolet™ iZ10 spectrometer equipped with EverGlo IR source, DLaTGS room temperature IR detector and single-bounce Smart Orbit™ accessory module with diamond ATR crystal. All hardware from Thermo Fischer Scientific Inc. (USA).

Each spectrum were averaged over 16 scans, taken at $4 \, cm^{-1}$ resolution, maximum detector window aperture and minimum interferometer mirror speed, in the range of $400 - 4000 \, cm^{-1}$. Background signal was averaged over eight scans prior to each measurement.

Collection of each spectrum, including background measurement, usually took around 2 min.

2.3. Data analysis

Analysis of collected spectra was carried out using the software suite accompanying the spectrometer, which included the OMNIC™ 9.1.27, used for data acquisition and single spectrum database comparison, the OMNIC™ Specta™ 2.0, used for multi-component deconvolution and database comparison, and the TQ Analyst™ 9.1.17, used for chemometric discriminant analysis. All software from Thermo Fischer Scientific Inc. (USA).

Spectral IR libraries had to be used for single- and multi-component sample spectrum analysis, as standards of target substances were not available for direct comparison. Libraries used included HR Comprehensive Forensic FT-IR Collection and HR Georgia State Forensic Drugs Library, available commercially from Thermo Fischer Scientific Inc. (USA), and the Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) Infrared Library [19], freely available on the internet. NBOMEs spectra were available only on the SWGDRUG library.

Single spectrum database comparison consisted in performing an automated search on all available spectra on the selected libraries to find the best single matches. Each single search took around 5 s. For multi-component deconvolution and database comparison, up to 4 of the available spectra on the selected libraries were automatically combined into one by the OMNIC™

Specta™ to produce the best matches possible, revealing the presence of other compounds other than the best single matches previously found. Each multi-component search took around 1 min. Finally, for discriminant analysis, a chemometrical method was created using the tools provided by the TQ Analyst™ software and used to classify the samples based on the collected spectra. The method contained a NBOME class constructed based upon spectra taken from blotters previously tested by ATR-FTIR and confirmed, by GC–MS or LC–MS, to contain at least one type of the NBOMEs previously detected (25B-, 25C- and 25I-NBOME, as showed on the results), which were used as class standards. Other classes, including a blank paper class, were created using the same procedure and the best available samples and added to the method. As target substances in pure form were not available to be used as class standards, sets of samples reproducing the observed behavior during the first two rounds of analysis (described on the results) were considered as best available samples and used to construct each class. Therefore, all classes for target substances were built using standards (samples) sharing the same type of matrix (paper). After calibration, performed automatically by the software, the resulting method were used to classify other samples not used as class standards. Though construction and calibration of the method took a couple of hours, including selection of best standard candidates for each class, after completion, classification of a new sample spectrum was virtually instantaneous.

3. Results and discussion

3.1. Single spectrum database comparison

As could be expected *a priori*, taking ATR-FTIR spectra directly from a blotter produced results matching primarily paper/cellulose on most samples analyzed, specially when the back side was tested. On the front side of some blotters, the presence of plastic polymers was detected, which was attributed to a protective film found covering the artwork, possibly created during painting/printing process. On a certain number of blotters, however, the collected spectra deviated considerably from the paper/cellulose and the plastic film profiles, indicating a strong presence of other substances. From all samples tested, both on back and front sides, blotters showing signals matching primarily 25B-NBOME, 25C-NBOME, 25I-NBOME and a mescaline-like compound were found. Comparative examples between spectra obtained from blotters and references are showed in Fig. 1 for 25I-NBOME and Fig. 2 for the mescaline-like compound.

Detection of such substances dominating the spectral profile while still impregnated on the paper suggests a very high dosage for these blotters.

At this primary level of analysis, NBOMEs were detected on 9 blotters, taken from 7 different cases, corresponding to 11.7% of the total number of blotters tested and 25.9% of apprehension cases. The mescaline-like compound was detected on 5 blotters, from 2 different cases, corresponding to 6.5% of blotters and 7.4% of cases. Negative results, matching paper/cellulose or plastic film were obtained on 63 blotters, from the 18 remaining cases, corresponding to 81.8% of total blotters and 66.7% of cases. Results obtained for each side of tested blotters are summarized on Table 1.

3.2. Multi-component deconvolution database comparison

After searching for the best single match on the available IR libraries, every blotter spectrum was submitted to deconvolution trough the multi-component database search engine available from the spectrometer software suite. On this second round of analysis, new matching spectra were constructed by mathematically combining up to four reference spectra available on the