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Application of a portable near infrared spectrometer for presumptive identification of psychoactive drugs

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ABSTRACT

A portable near infrared spectrometer was applied to the presumptive identification of psychotropic drugs based on library searching. Data-treatment methods (mathematical pretreatment and library search algorithm) were examined on the basis of differentiation ability. The optimized mathematical pretreatment was a standard normal variate followed by the 2nd derivative. The correlation coefficient showed the best differentiation ability in the library search algorithms. Optimized data-treatment was effective for minimizing the effect of particle size on identification. The optimized data-treatment methods were validated by the spectra of psychotropic substances (n = 120). Identification criteria for the psychotropic drugs were decided on the basis of the results of the validation. As a consequence, 8 out of 11 forensic samples containing psychoactive substances were able to be positively identified. Thus, the portable near infrared spectrometer with optimized data-treatment processing is a useful tool for rapid screening and presumptive identification of seized materials.

1. Introduction

Recently, many kinds of new psychoactive substances (so-called legal-high) have been circulating in the illicit drug market. In most forensic science laboratories, gas chromatography/mass spectrometry (GC/MS) is the first choice for analysis of powdered or crystallized drugs because of its excellent separation and identification ability. However, GC/MS requires time-consuming chromatographic separation. In addition, differentiation of positional isomers by GC/MS is often challenging because of similarities of retention times and mass spectra. For example, the freebases of 4-fluoromethcathinone (4-FMC) and 3-fluoromethcathinone (3-FMC) exhibit similar retention times and mass spectra [1].

Optical spectrometries such as mid-infrared (mid-IR) spectrometry and Raman spectrometry are also widely used for analysis of drugs. The Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) categorized mid-IR and Raman spectrometries as category A, which means these techniques are amongst the techniques with the maximum potential discriminating power [2]. The discrimination ability for positional isomers is often superior to GC/MS. For example, mid-IR spectrometry can readily differentiate 4-FMC and 3-FMC [1].

Near infrared (NIR) spectrometry is another important optical technique. The NIR region extends from about 780 nm to 2500 nm [3]. This region corresponds to that between the red end of the visible spectrum and the beginning of the mid-IR region [3]. NIR absorbance corresponds to overtones or combinations of molecular vibrations that have their fundamental absorptions in the mid-IR region [3], therefore, NIR spectra can provide similar information to mid-IR and Raman. NIR spectrometry, however, has some advantages over mid-IR and Raman spectrometries. Weak absorption in the NIR region, unlike that for the mid-IR region, enables one to obtain spectra by diffuse reflection without sample dilution and even through a plastic holder [4]. Raman spectrometry can also detect materials contained in a plastic holder [5], however, Raman spectra of visibly colored samples are often subject to interference by laser-induced fluorescence. In contrast, NIR spectra are not influenced by sample color.

NIR spectra are featureless in comparison with mid-IR and Raman spectra. Initially, the lack of spectral detail has made application to the identification of chemical substances difficult. However, with the advent of computer-aided data analysis the situation has changed and NIR spectrometry is specified in the pharmacopoeias of Europe, the United Kingdom, and Japan [6–8].

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In the pharmaceutical industry, the technique is often applied to the identification of raw materials. However, in the field of forensic drug analysis, there were only two reports on the identification of the drugs. One report was visual comparison of the NIR spectra of some medicines (diazepam, flunitrazepam, and methadone hydrochloride) [9]. This approach is not suitable for comparison of many spectra. The other report identified authentic standards of 37 compounds including drugs of abuse on the basis of similarity [10]. This article was published more than 20 years ago, before the development of computer-aided data analysis. Most of the recent forensic applications of NIR spectrometry were quantification of specified drugs such as MDMA [11–14], heroin [15,16], cocaine [17] using multivariate analysis. Multivariate analysis is appropriate for quantification or grouping of the samples but not always for identification of unknown samples, because a new model must be built when a new substance is added to the spectrum library.

The aim of this study was to apply a portable NIR spectrometer to the presumptive identification of psychotropic substances based on library searching. Specifically, optimization of data-treatment methods (mathematical pretreatment and library-search algorithm), decision on the criteria for positive identification, and validation of the criteria with reference to forensic samples containing psychoactive substances are reported on and discussed.

2. Materials and methods

2.1. Samples

2.1.1. Standard samples

The powder or crystalline form of standard samples was divided into two categories: psychoactive substances (including their isomers) (Table 1, 120 compounds) and non-psychoactive substances (Table 2, 30 compounds). Classes of the psychoactive substances were phenethylamines (42 compounds), cathinones (43 compounds), tryptamines (13 compounds), piperazines (10 compounds), synthetic cannabinoids (5 compounds), and miscellaneous (7 compounds). Non-psychoactive substances were sugars (15 compounds), other organic (6 compounds), and inorganic (9 compounds) compounds. Typically, these latter substances were diluents in seized materials or medicinal tablets, or readily available white powder.

2.1.2. Forensic samples

Table 3 lists the 11 forensic samples used for validation of the criteria for positive identification. Sample B was seized in Japan. The other samples were obtained as "legal high" via the Internet or from retail shops prior to the introduction of new sales regulations. Drugs contained in the samples were identified by GC/MS. No additional peaks, except those for each specific drug, were observed in the GC/MS chromatograms.

2.2. Measurement of NIR spectrum

NIR spectra were measured using a portable NIR spectrometer (Model-C, Systems Engineering, Tokyo, Japan), featuring AOTF Analyzer (Systems Engineering) software. The NIR spectrometer was equipped with a tungsten-halogen lamp, an Acousto-Optic tunable filter for wavelength selection, and a lead sulfide detector. The beam diameter was 1 mm. Spectra were collected over the range of 1400–2400 nm with 1001 data points. The data were automatically converted to spectra covering the range of 1401 to 2360 nm (1001 points) by Discrim (Systems Engineering) software. The purpose of this conversion was to enhance compatibility with the spectra obtained by other NIR spectrometers. Each spectrum was determined by averaging 10 scans. A ceramic standard served as a reference sample.

The samples were mounted on an aluminum tray without any pretreatment, such as pulverization or classification based on particle size, unless stated otherwise. The spectra were recorded in diffuse reflection mode. The spectra of the psychoactive substances were measured three times with the samples being stirred between each measurement. The spectra of the non-psychoactive substances and the forensic samples were measured once.

A spectrum library was constructed from the spectra of the standard samples of the psychoactive substances (360 spectra, from 120 compounds) and the non-psychoactive substances (30 spectra, from 30 compounds).

2.3. Optimization of data-treatment methods

Data-treatment methods, which consisted of mathematical pretreatment and a library search, were examined to maximize the differentiation ability between substances. Mathematical pretreatment methods were first examined; thereafter, library search algorithms were examined using the spectra, which were pretreated mathematically by the optimized method.

2.3.1. Mathematical pretreatment of NIR spectra

Mathematical pretreatment of the acquired raw spectra was performed by the AOTF Analyzer. Four pretreatment methods (non-pretreatment, standard normal variate (SNV) transformation, 2nd derivative, and SNV transformation followed by the 2nd derivative (SNV + 2nd derivative)) were tested. The 2nd derivative was performed by the Savitzky–Golay method (2 degree polynomial and 19 data point smoothing). Similarity was calculated on the basis of Euclidean distances by the AOTF Analyzer.

2.3.2. Library search of the pretreated NIR spectra

The spectral data (*.csv file) pretreated by the AOTF analyzer were subsequently exported into Panorama Search 1.1 (LabCognition, Dortmund, Germany) software, which was developed for data analysis of mid-IR spectra. After normalizing the pretreated spectra to the highest peak intensity, similarity was calculated on the basis of four library search algorithms (difference, squared difference, correlation coefficient, and scalar product).

2.3.3. Evaluation of the mathematical pretreatment method and the library search algorithm

A single spectrum for each of the five psychoactive substance (MDMA HCl, 4-MMC HCl, MDMA phosphate, cocaine HCl, and DPT HCl) was used as a test spectrum to optimize the data-treatment. The optimal data-treatment methods were selected on the basis of discrimination ability from the other substances. The ability was evaluated by the "α score", which was calculated from the library search results as:

$$\alpha \text{ score} = \frac{A - B}{A - C}$$

where A is the similarity to the query spectrum itself; B is the lowest similarity to the same substance as the query spectrum; and C is the highest similarity to a different substance from the query spectrum. A lower α score indicates a better discrimination between the test substance and the others. When the α value is ≥ 1, this means that a substance, indistinguishable from the test sample, is present.

Fig. 1 shows an example of a calculation of the α score. In this case, A, B, and C were 0.9911, 0.9879, and 0.9710, respectively, and the α score was calculated to be 0.159.