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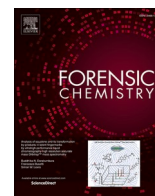
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The importance of wavelength selection in on-scene identification of drugs of abuse with portable near-infrared spectroscopy

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ABSTRACT

Both the increasing volume and diversity of drugs-of-abuse encountered by investigation services necessitates the need for fast on-scene detectors to detect and identify a broad range of substances. Near-Infrared (NIR) spectroscopy is suitable for presumptive drugs testing by miniaturized sensors implemented in portable devices. Currently, a myriad of different portable NIR spectrometers is available that utilize different wavelength ranges. This study presents a comparison of NIR spectra of frequently occurring drugs analyzed by five different devices. A 350 – 2500 nm range laboratory grade VIS-NIR spectrometer was used to gain insight in spectral ranges diagnostic for substances relevant in forensic science. Obtained spectra were compared to the output of portable spectrometers operating in the 740 – 1070 nm, 950 – 1650 nm, 1550 – 1950 nm and 1300 – 2600 nm range. The results yielded novel insights in the usability of individual spectrometers by visual inspection of NIR spectra as well as comparative statistics with reference substances. For MDMA detection, an instrument capable of detecting a highly abundant and specific peak at 2020 nm is beneficial whereas colored samples are more difficult to detect by lower wavelength range sensors. Relatively pure, lightly colored samples may be correctly characterized by all sensors. These findings may aid NIR spectrometer selection in forensic practice as well as future studies on instrument selectivity or cross-platform calibration transfer.

Introduction

Investigative authorities, such as the police or border security, require rapid and reliable methods for the on-scene detection of illicit drugs. The traditional way of on-scene presumptive testing for drugs-of-abuse is by colorimetric spot tests that are based on chemical reactions. These disposable tests use concentrated strong acids and metal salts; therefore resulting in both safety risks for the operator and producing hazardous waste. In addition, the scope of colorimetric tests is limited to a small number of common illicit drugs [1]. The emergence of hundreds of new synthetic designer drugs, so-called new psychoactive substances (NPS) in the illicit drug market [2], therefore, raised the need for on-scene detection techniques with a higher sensitivity and selectivity

and a broader and more flexible scope.

Spectroscopic techniques fulfil these requirements as associated spectra are *i.* sufficiently specific for identification of individual substances, *ii.* spectra for novel substances could be easily added to a spectral database, *iii.* the analysis is non-destructive, and *iv.* generated by a non-disposable instrument, thus only requiring a one-time investment. Spectroscopic techniques with applications in on-scene forensic drug detection are Raman spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy and Near-Infrared (NIR) spectroscopy [3,4]. Unlike Raman and FTIR, NIR spectroscopy is considered relatively limited in terms of direct chemical information that is available in the spectra, because of the interrogated wavelength range. In NIR, the obtained signal originates from multiple vibrational overtones or combination

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bands, typically in the range of 1000 – 2500 nm [5]. An advantage of NIR spectrometers over other spectroscopic techniques is that they are relatively low cost and small sized due to silicon based detectors combined with low-energy consuming light sources. The small size allows the implementation in handheld or even pocket-size devices [6,7]. Furthermore, NIR sensors in diffuse reflection mode are flexible in application to diverse matrix interfaces, so they can be applied as a point-and-shoot device without sample preparation [6].

Several studies have reported the use of NIR for forensic drugs-of-abuse testing; both on benchtop laboratory grade instruments [8–10] as well as portable devices for on-site testing [11–16]. Most benchtop NIR instruments operate in the full NIR-wavelength range from ~ 800–1000 nm to ~ 2500 nm, however, the smaller portable NIR devices interrogate various more confined parts of the NIR spectrum. For example, Hesperhol *et al.* [14] demonstrated cocaine detection on a 900 – 1700 nm nanoNIR instrument. Risoluti *et al.* [13] and Correia *et al.* [15] both used the slightly narrower 950 – 1650 nm wavelength range MicroNIR instrument for illicit-drug detection using Partial Least Squares (PLS) based multivariate statistical models. This same instrument was also incorporated in the NIRLAB architecture for rapid drug testing using cloud-based central data storage and mobile applications; as reported by Copepy *et al.* [12]. Additionally, Tactiscan recently introduced a similar cloud-based NIR platform for usage by police forces in which the 1550 – 1950 nm NIRone S2.0 sensor from Spectral Engines is integrated [17,18]. This sensor only slightly overlaps in spectral range with the MicroNIR. In earlier work, our group investigated the performance of a confined wavelength range 740 – 1070 nm sensor for cocaine detection [11]. The differences in wavelength range used among these studies justify a further investigation into the importance of wavelength range in on-scene drugs of abuse detection with portable NIR spectroscopy.

In this study, we present a spectral and statistical comparison of five NIR spectrometers all operating in a different wavelength range. Spectra of commonly encountered illicit drugs, common adulterants, new psychoactive substances (NPS), and seized tablets containing either 3,4-methylenedioxymethamphetamine (MDMA) or other synthetic drugs were used to test the capabilities of these instruments for forensic drug detection. Comparative statistics were applied to match spectra of five types of commonly encountered drugs in street samples to their chemically pure reference compounds, being cocaine (HCl and base), methamphetamine, amphetamine, ketamine and MDMA. The identification of MDMA was performed on powder of crushed colored tablets in a glass vial as well as on intact colored tablets in a standard issue grip bag. In this way, the importance of the wavelength range of the NIR spectrometer chosen for the identification of a certain drug of abuse could be assessed under realistic practical conditions. The data provided an understanding of compound and wavelength specific selectivity and thus optimal spectrometer selection for NIR-based approaches in forensic illicit-drug detection. These findings provide interesting leads for future research on NIR-based illicit drugs detection; such as the possibilities for transfer of high resolution spectra from benchtop, laboratory grade primary instruments to multiple portable sensors with lower resolution and more confined wavelength ranges for application-specific on-scene detection.

Materials and methods

Chemicals and reagents

Cocaine HCl, cocaine base, heroin HCl (white heroin), heroin base containing case sample (brown heroin), MDMA HCl, amphetamine sulphate, methamphetamine HCl, ketamine, 2-(4-Bromo-2,5-dimethoxyphenyl)ethanamine HCl (2C-B), gamma-hydroxybutyrate (GHB) sodium salt; the NPS 2-methylmethcathinone (2-MMC), 3-methylmethcathinone (3-MMC), 4-methylmethcathinone (4-MMC), 3-methylethcathinone (3-MEC), 4-methylmethcathinone (4-MEC) and 3-

chloromethcathinone (3-CMC) as HCl salts were all provided by the Amsterdam Police forensic laboratory and originated from seized high purity casework samples. The adulterants acetylsalicylic acid, caffeine, inositol, lactose, levamisole, lidocaine, mannitol, paracetamol, phenacetin and procaine were obtained from different suppliers as reported in earlier work [11]. For statistical comparison, a set of over 157 casework samples consisting of a wide variety of substances was used for matching with cocaine HCl, cocaine base, amphetamine, methamphetamine and ketamine references. If not already in powder form, samples were crushed to powder in a mortar. For comparison with MDMA, a set of 71 seized tablets was used of which 39 tablets contained MDMA and 32 tablets contained other psychoactive substances. Both the intact seized tablets in plastic low-density polyethylene (LDPE) grip bags were used, as well as the crushed tablets in glass vials. The ecstasy tablets originated from independent seizures with visually different imprints and color. Full details and pictures of these tablets are reported elsewhere [19].

NIR spectrometers and data acquisition

The whole sample set was analyzed by the NIR spectrometers listed in Table 1 by placing glass vials with powdered sample material directly on top of each sensor. For the statistical comparison of MDMA in seized street samples, intact ecstasy tablets were also measured inside a plastic LDPE grip bag. The plastic grip bag with the tablet was placed directly on the sensor heads of spectrometers. The number of replicates as indicated in Table 1 was based on the analysis time and the number of ways a sample could be placed on the sensor head.

The NeoSpectra (Si-Ware, Cairo, Egypt) [20], NIRone S2.0 (Spectral Engines, Steinbach, Germany) [18], MicroNIR (Viavi Solutions, Scottsdale, AZ, USA) [21] and SciO (Consumer Physics, San Fransisco, CA, USA) [22] all were spectrometers designed for use in portable (handheld, tabletop) applications and operated via 5 V USB or a built-in battery. The ASD LabSpec4 (Malvern Panalytical, Malvern, UK) [23] was designed as a laboratory grade benchtop NIR and required a 230 V AC connection. All instruments employ a different NIR wavelength range, with the ASD LabSpec covering the most extensive part of the visible (VIS) and NIR spectrum with the highest resolution of 1 nm/datapoint and a reported resolution of 10 nm FWHM at 1400 and 2100 nm [23]. Table 1 shows both the resolution stated by the manufacturers and the average wavelength range per datapoint. It must be noted that the resolution of the sensors was reported in different ways due to differences in detection technology, therefore, hampering straight forward comparison. The number of data points obtained in the raw data (Table 1) also does not necessarily reflect the actual spectral resolution. For the NIRone sensor (1550 – 1950 nm), it is noteworthy that the manufacturer also provides four other system configurations that operate in different wavelength ranges, *i.e.* 1100 – 1350 nm, 1350 – 1650 nm, 1750 – 2150 nm and 2000 – 2450 nm. Exported raw data for the ASD, NeoSpectra, NIRone and MicroNIR were in absorption units. Raw data for the SciO were reported in %Reflected light. For comparison, SciO data was transferred to absorption by calculating the negative logarithm.

Data analysis

Unscrambler X 10.3 (Camo Analytics, Oslo, Norway) was used for data import, visualization and preprocessing (averaging of sample replicates). Calculations to obtain statistical match scores of the NIR spectra of the six reference compounds with the seized street samples were performed in R version 4.0.2 (R Foundation for Statistical Computing, Vienna, Austria) [24] using RStudio version 1.4.1717. R-packages prospectr_0.2.0 [25], signal_0.7–6 [26], mdatools [27] and pracma [28] were used.

For obtaining statistical match scores, the first-derivative of the NIR spectra were calculated, using a second-order polynomial fit and filter lengths were chosen to effectively suppress noise for each sensor. For the

Table 1

Characteristics of the NIR spectrometers used and individual sample replicates recorded in this study.

device	wavelength range	dp (#)	nm/dp	resolution (FWHM)	instrument size	replicates (#)
ASD LabSpec4	350–2500 nm ^a	2151	1.0	10 nm	130 × 370 × 290 mm	2
Si-Ware NeoSpectra	1300–2600 nm	160	8.1	16 nm	32 × 32 × 22 mm	3
Spectral Engines NIRone S2.0	1550–1950 nm	201	2.0	15–21 nm	25 × 25 × 18 mm	3
Viavi Solutions MicroNIR	950–1650 nm	125	5.6	12.5 nm	47 mm ϕ × 50 mm	3
Consumer Physics SCiO	740–1070 nm	331	1.0	n.a.	54 × 36 × 15 mm	5

dp: datapoints; resolution as stated by the manufacturer; n.a.: not available; FWHM: full width at half maximum; a: for obtaining statistical match scores, the wavelength range of 1000 – 2500 nm was used for the ASD LabSpec4.

ASD, the spectral range of 1000 – 2500 nm was used to eliminate the influence of non-diagnostic sample color at lower wavelengths. Filter lengths were set as following: 43 datapoints (dp), corresponding with ~ 43 nm (ASD), 5 dp, ~41 nm (NeoSpectra), 21 dp, ~40 nm (NIRone), 7 dp, ~36 nm (MicroNIR), 43 dp, ~43 nm (SCiO). Subsequently, for each first-derivative reference spectrum, the spectral features were identified using a generic peak-finder algorithm (pracma). An example of this is shown in **Figure S1** in the Supplemental Information for a ketamine reference in which 69 spectral features were identified for subsequent use. The total number of spectral features for the common drugs discussed in this study can be found in **Table S1**. Match scores were then calculated as Pearson's correlation between the references' (1st derivative) peak maxima/minima intensity value and the values at the corresponding wavelength points of each unknown spectrum. Match scores generally ranged from 1.00 (perfect match) to 0.00 (no similarities at all). Scores with lower values than 0.00 were also observed and were interpreted as 'absence of any similarity'. Based on the match scores, an optimal decision value for each drug of abuse was set to obtain the lowest false positive (FP) and false negative (FN) rates in the sample set.

Results

Spectral range differences

The ASD was used as the broad-range standard to get insight into the VIS-NIR spectra of drugs-of-abuse substances. Full range spectra for MDMA HCl, amphetamine sulphate, cocaine base and cocaine HCl are shown in **Fig. 1**. In general, the highest absorbance in NIR signals were observed in the higher wavelength range between 1700 and 2500 nm (viz. 5900 – 4000 cm^{-1}). This is the first overtone and combination band region of the NIR spectrum that originates from vibration and rotation bands in the IR region [5,15]. In the second overtone (1100 – 1600 nm; 9.100 – 6.250 cm^{-1}) and third overtone (700 – 1100 nm; 14.250 – 9.100

cm^{-1}) regions, additional diagnostic spectral signals for individual compounds were also observed, although decreasingly abundant towards lower wavelengths. In general, the width of higher order overtone peaks increases as can clearly be observed in **Fig. 1**. Consequently, the instrument's resolution at short wavelengths is less critical, while the specificity of NIR measurements at long wavelengths (2000 – 2500 nm) significantly benefits from high resolutions. For compound identification, sharp peaks with large $\Delta A/\Delta \text{nm}$ (difference absorption/wavelength region) are helpful since such intrinsic molecular properties help to improve the signal-to-noise of the measurement. The spectral range for all NIR spectrometers included in this study is indicated by colored bars in **Fig. 1**. This already provides a first insight with respect to the potential selectivity differences that may be encountered for different instruments. For example, the major ~ 2000 nm peak for MDMA is only detectable with the ASD and the NeoSpectra as this peak falls outside the range of the other instruments. Especially this peak was found highly diagnostic for MDMA as a wide range of drugs, pharmaceuticals and cutting agents (**Figures S2 – S4**) did not exhibit a strong absorption at this wavelength. This signal is related to crystal water in MDMA and the diagnostic nature of this spectral feature is currently further investigated in our group. The value of this 'MDMA peak' is further discussed in the section on colored samples.

The comparison of spectra obtained from the various spectrometers is shown in **Fig. 2** for the common drugs of abuse cocaine, ketamine, MDMA and methamphetamine (all as hydrochloride salts). Similar comparisons for cocaine (as free base), amphetamine sulphate, GHB sodium salt, 2C-B and heroin (both as hydrochloride salt and a casework sample containing heroin base) can be found in **Figure S2** in the Supplemental Information. It is noteworthy that in NIR, in line with other spectroscopic techniques, the free base and various salt forms of drugs yield different spectra and must thus be considered as independent substances in libraries and chemometric modelling [29]. Spectral comparisons for the common pharmaceuticals and adulterants paracetamol,

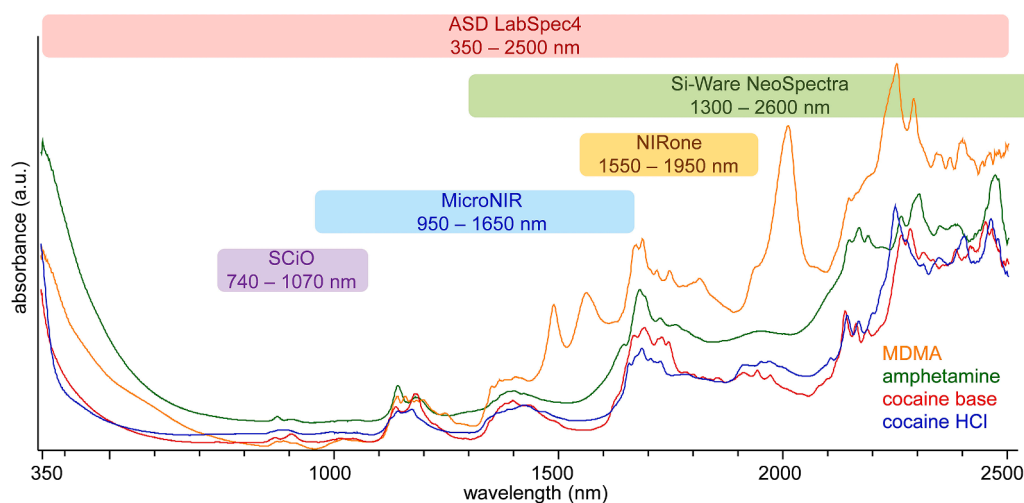


Fig. 1. The high resolution VIS-NIR spectra of four common drugs of abuse with an illustration of the wavelength ranges covered by the portable spectrometers that are tested in this study. Spectra recorded with the ASD LabSpec4 spectrometer.

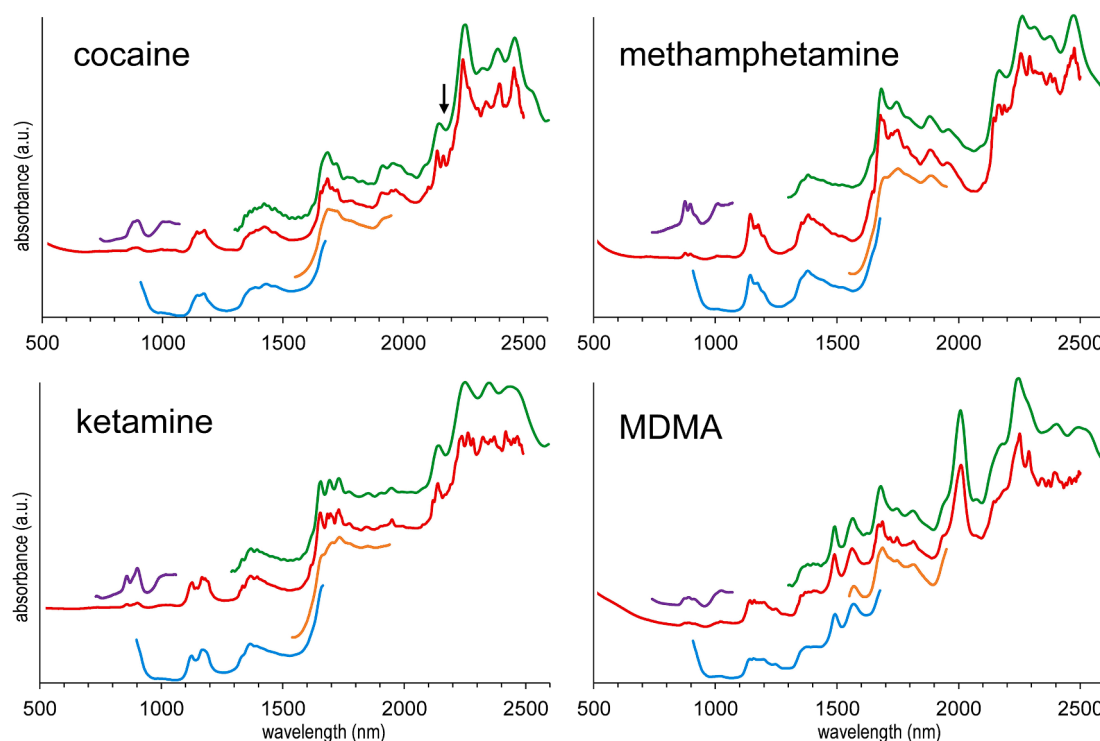


Fig. 2. Comparison of the spectral output for common illicit drugs (all as HCl salt) from the different sensors. red: ASD LabSpec4; green: NeoSpectra; orange: NIRone; blue: MicroNIR; purple: SCiO. The arrow indicates the example of resolution differences described in the text.

levamisole, acetylsalicylic acid, lidocaine, caffeine, phenacetin, procaine, mannitol, lactose and inositol are shown in [Figure S3](#). [Figure S4](#) depicts the NIR spectra for the NPS 2-MMC, 3-MMC, 4-MMC, 3-MEC, 4-MEC and 3-CMC. From all these figures, it becomes clear that spectra recorded by different spectrometers are quite consistent and thus comparable in terms of the presence and relative abundance of spectral features. The three adjacent peaks diagnostic for MDMA between 1400 and 1750 nm ([Fig. 2](#)) are, for example, distinguishable in the obtained spectra from the ASD and NeoSpectra. Only the two lowest wavelength peaks (1490 nm and 1570 nm) are detectable by the MicroNIR. The 1570 nm peak can also be observed at the beginning of the NIRone spectrum, as well as the third 1685 nm peak. The first peak was not detectable by this sensor as it falls outside the spectral range for its detector. It is also noticeable that the spectral selectivity that may be expected for a certain sensor can be different amongst individual substances. For instance, the distinctive doublet peak shape \sim 1750 nm for GHB ([Figure S2](#)) can only be detected by the NIRone, NeoSpectra and ASD making these potential instruments of choice for identification of this substance.

Additionally, the obtained spectra provide insights into resolution differences between the spectrometers. According to the fine spectral detail observed in the ASD data, this benchtop instrument was found superior. For example, two narrow peaks and a shoulder could be distinguished \sim 2150 nm in the ASD spectrum for cocaine HCl ([Fig. 2](#), red plot), whereas this level of detail was lost in the NeoSpectra signal ([Fig. 2](#), green plot) leaving only a single broad peak. Similarly, the NeoSpectra shows more spectral details than the NIRone (orange) as becomes apparent especially from the spectra of ketamine, heroin and GHB ([Figure S2](#)). Overall, the absorption bands and raw spectral pattern were similar for all instruments. However, the level of spectral fine structures was less detailed due to the lower resolution of the portable spectrometers. This observation provides interesting opportunities for future research in on-scene drug detection, such as calibration transfer between different sensors or emulation of reference spectra databases derived from the full-range high resolution NIR spectra obtained by a

benchtop instrument [30–32]. In order to facilitate such developments, our raw spectral dataset is made available as a separate data article.

Spectral selectivity for white powders and limitations for mixtures

The relatively less abundant spectral peaks in the lower wavelength ranges for white colored drugs of abuse do not necessarily reflect a limited spectral selectivity and reduced usefulness in a forensic setting. Despite being less intense in comparison to peaks at other wavelengths, specific and reproducible spectral signals may suffice for detection and identification when sufficiently distinguishable from signals of other substances. Examination of replicate scans gives insight into the spectral specificity for common drugs. Data were normalized (*i.e.* standard normal variate, SNV, preprocessing) to compensate for absolute intensity differences that may originate from the physical properties of the sample. [Fig. 3](#) shows overlays of three replicate scans for cocaine, heroin, MDMA, and methamphetamine analyzed on all five spectrometers. It must be noted that the abscissa depicting the wavelength varies in both scaling and range for individual instruments. In panels A (ASD) and B (NeoSpectra) of [Fig. 3](#), the spectra of MDMA and heroin could be easily recognized by the presence of the distinctive peaks at 2020 nm and 1980 nm, respectively. Although not present in the spectra from the NIRone (panel C) and MicroNIR (panel D), these drugs of abuse could still be distinguished by multiple other characteristic spectral features or the overall pattern of the signal. Only for the SCiO (panel E), limitations were encountered as depicted for heroin in which the three replicate scans yielded major differences. The probable explanation is the fact that the SCiO wavelength range partially overlaps with the UV-VIS range in which constituents of the heroin sample also show absorption. This effect can be seen in the 500 – 1000 nm range of the ASD spectra for both ‘brown’ and ‘white’ heroin ([Figure S2](#)) by the strong increase at the low wavelength end of the spectrum. The entire wavelength range of the SCiO falls within the slope of this peak.

Forensic samples of illegal drugs are typically mixtures with a relatively high (*i.e.* > 25 wt%) active ingredient content. The presence of

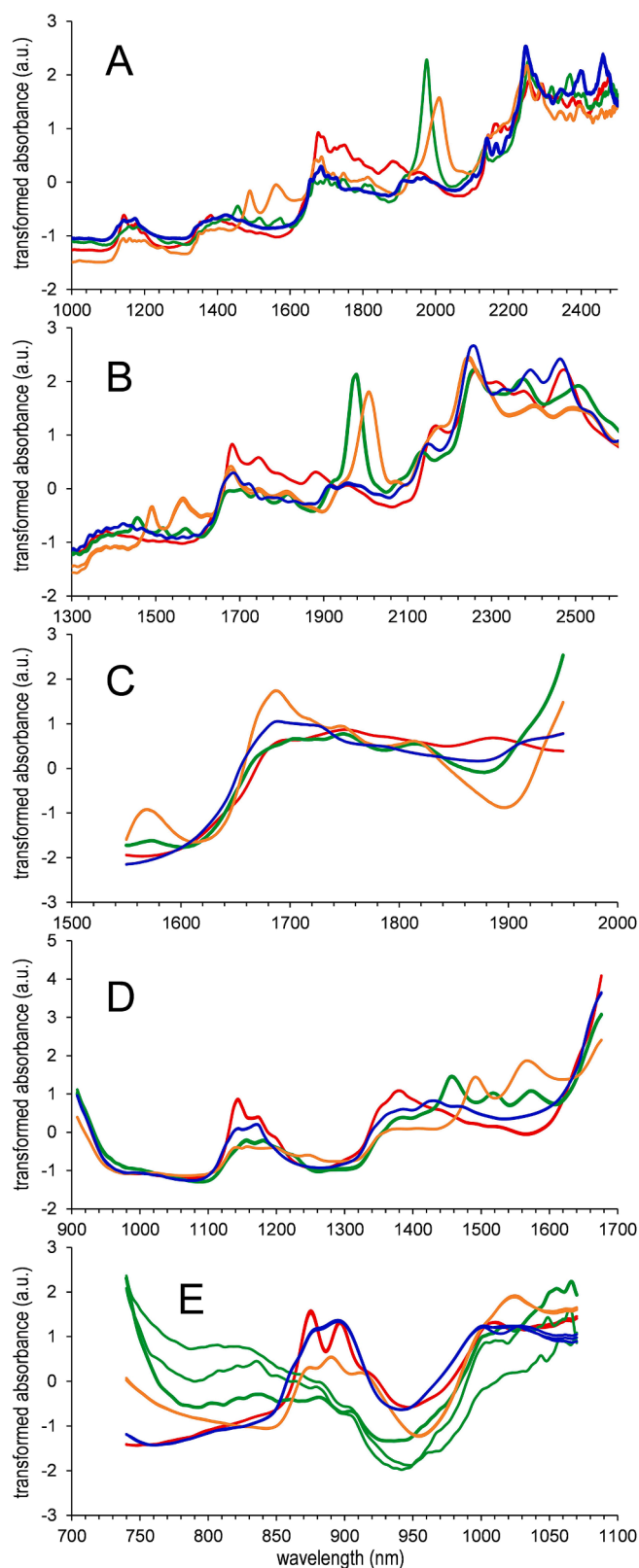


Fig. 3. Standard Normal Variate (SNV) preprocessed data of three replicate scans of four common drugs on all spectrometers. A: ASD LabSpec4; B: NeoSpectra; C: NIRone; D: MicroNIR; E: SCiO. Substances: cocaine HCl (blue); MDMA (orange); heroin HCl (green); methamphetamine (red).

adulterants or excipients will affect the obtained spectral signals and may therefore hamper drug detection. To allow for a more quantitative assessment of the effectiveness of the five NIR spectrometers to identify illicit substances, NIR reference spectra of five commonly found street drugs were statistically compared to a wide variety of seized street samples (Table 2). This casework sample set included common illicit drugs at various degrees of adulteration, new psychoactive substances and uncontrolled substances such as cutting agents, pharmaceuticals and common household chemicals (details and results per sample can be found in the Supplemental Information). The obtained Pearson's correlation match score ranges for all positives provide a first indication of the sensor's suitability to identify a certain compound. For example, methamphetamine samples returned a high > 0.97 match score in all cases on all spectrometers. Because other substances yielded a score well below this (e.g. cocaine gave scores of 0.56 on the ASD, 0.79 on the NeoSpectra and 0.87 on the MicroNIR) a decision threshold value around 0.95 suffices for 100% correct detection of methamphetamine on all spectrometers. Contrary, amphetamine was found much more challenging with (true positive) match scores for seized amphetamine-containing samples ranging between ~ 0.99 for relatively pure samples and 0.40 for more diluted samples. The explanation for this is threefold: *i.* amphetamine casework samples are typically diluted with caffeine and/or paracetamol levels that exceed 50 wt%, *ii.* seized amphetamine often appears in paste or coarse chunks rather than powders and *iii.* the amphetamine sulphate NIR spectrum (Figure S2) does not show characteristic diagnostic spectral peaks. The number of FP and FN results provide insight in the usability of a certain sensor for a given substance. For cocaine (both as HCl and base) the sum of FP and FN results increases for the sensors operating in a lower wavelength range, thus being best (only 2 FN) for the ASD and worst (32 FPs and 7 FNs) for the SCiO. However, as an overall result, detection of most substances seemed possible with all instruments for this set of lightly colored powdery samples. It must be noted that the presented models are only to provide an indication of the optimal NIR range(s) for a certain compound to be detected. Due to its generic nature, this model is not optimized for each individual spectrometer, with the exception of the filter length to calculate the derivative. The presented results thus should not be considered optimal for the detection of the illicit-drugs in casework samples and chemometric models optimized for a specific sensor and substance may considerably increase performance.

In line with the model results in Table 2, the spectra in Fig. 3 as well indicate that chemometric models aiming for the identification of drugs of abuse in relatively pure, lightly colored (e.g. white, colorless) powders may be successful for all spectrometers included in this study. It may, however, be expected that more advanced data preprocessing methods and chemometric models are required for instruments operating in an area with less intense NIR signals and a consequently lower signal-to-noise ratio. The same may be true for the identification of substances that do not yield diagnostic spectral peaks within a certain NIR range. These more advanced models may require larger training sets, more extensive preprocessing or the use of multiple multivariate or machine learning models. In earlier work, our group demonstrated cocaine detection by the SCiO pocket-size spectrometer [11]. Despite its low and confined wavelength range, a multi-stage model based on a 10,000+ scans training set nevertheless enabled robust cocaine detection using this sensor.

Limitations for colored samples

Especially MDMA is frequently encountered in a large variety of differently colored ecstasy tablets. Besides MDMA, these tablets contain excipients (for example lactose, cellulose) and coloring agents. A total of 39 different MDMA-containing ecstasy tablets were crushed and subsequently analyzed on all 5 spectrometers to examine the influence of these excipients and colorants. The obtained raw spectral signals are shown in the first column of Fig. 4. The line color of each spectrum

Table 2

Performance comparison of the five spectrometers for identification of 5 drugs of abuse in seized street samples.

	Active ingredient	ASD	NeoSpectra	NIRone	MicroNIR	SCiO
Cocaine HCl	Avg Score (Range)	0.95 (0.99–0.72)	0.96 (0.99–0.81)	0.97 (1.00–0.65)	0.96 (0.99–0.80)	0.97 (0.99–0.90)
	Decision value	0.72	0.80	0.90	0.80	0.90
	FP (total negatives in set)	0 (1 18)	4 (15 6)	3 (15 8)	6 (15 3)	9 (1 26)
	FN (total Coc HCl in set)	2 (39)	2 (41)	3 (41)	4 (40)	5 (40)
Cocaine base	Avg Score (Range)	0.96 (1.00–0.73)	0.97 (0.99–0.87)	0.98 (1.00–0.87)	0.99 (1.00–0.97)	0.98 (1.00–0.89)
	Decision value	0.70	0.87	0.87	0.97	0.89
	FP (total negatives in set)	0 (1 33)	1 (17 3)	0 (17 4)	0 (17 0)	23 (1 42)
	FN (total Coc base in set)	0 (24)	0 (25)	0 (25)	0 (25)	2 (25)
Amphetamine	Avg Score (Range)	0.60 (1.00–0.09)	0.69 (1.00 - <0.00)	0.88 (1.00–0.55)	0.78 (1.00–0.07)	0.55 (0.98 - <0.00)
	Decision value	0.90	0.90	0.97	0.98	0.98
	FP (total negatives in set)	0 (1 51)	0 (19 0)	0 (19 1)	0 (18 6)	0 (1 58)
	FN (total Amph in set)	4 (6)	4 (7)	4 (8)	4 (8)	4 (7)
Methamphetamine	Avg Score (Range)	0.99 (1.00–0.97)	0.99 (1.00–0.98)	0.99 (1.00–0.97)	0.99 (1.00–0.99)	0.99 (1.00–0.98)
	Decision value	0.95	0.95	0.97	0.95	0.98
	FP (total negatives in set)	0 (1 55)	0 (19 4)	0 (19 5)	0 (19 0)	0 (1 61)
	FN (total MethAmph in set)	0 (2)	0 (4)	0 (4)	0 (4)	0 (4)
Ketamine	Avg Score (Range)	0.98 (1.00–0.88)	0.98 (1.00–0.88)	0.97 (1.00–0.79)	0.98 (1.00–0.87)	0.97 (1.00–0.76)
	Decision value	0.74	0.78	0.88	0.98	0.99
	FP (total negatives in set)	0 (1 46)	0 (18 6)	0 (18 7)	0 (18 2)	2 (1 53)
	FN (total Keta in set)	0 (11)	0 (12)	1 (12)	2 (12)	2 (12)

resembles the actual color of the ecstasy tablet to visualize the effect of the colorants. The bold black line in all panels represents the reference spectrum of pure MDMA. Logically, all colored tablets absorbed light in the visual range as notable in the 500–750 nm part of the ASD spectrum (Fig. 4A-raw). For the typical colors of ecstasy tablets (e.g. blue, green, yellow, pink, orange, red), this absorption was most abundant in the part of the spectrum below 1000 nm. For these tablets, spectral signals originating from MDMA remained visible in the 1000–1500 nm range, although less intense. Contrary, several gray, brown, and black colored tablets showed strong absorption over the entire NIR wavelength range. For these tablets, the diagnostic features for MDMA were hardly visible in the raw spectrum. Although it is obvious that the sensors operating at the lowest wavelengths are most severely impacted by this effect, illicit substance detection with NIR is in general cumbersome for dark colored specimens as the transmittance and reflectance is limited over the entire wave length range. For the SCiO (Fig. 4E), absorption from colorants was significantly more apparent than the absorption from MDMA itself. In line with the white powdered drugs, the SNV preprocessed spectra were assessed with an additional focus on the differences and similarities of the spectral features. The second column in Fig. 4 shows the corresponding SNV processed spectra for all five spectrometers. It must be noted that the < 1000 nm part of the ASD spectrum was excluded for SNV to limit the impact of the tablet color. In addition, the spectra of the dark gray/black ecstasy tablet, marked with an asterisk in the first column of Fig. 4 were excluded for the readability of the figure. The SNV processed spectra convincingly show the differences in selectivity for MDMA detection among the five instruments. Again, the high abundant 2020 nm peak for MDMA proved meaningful as this peak -after SNV- was visible in all spectra irrespective of color. This peak can only be detected by the ASD (Fig. 4A) and NeoSpectra (Fig. 4B). A less abundant, but similarly selective peak was observed at 1490 nm in the spectra recorded with the MicroNIR (Fig. 4D). The NIRone (Fig. 4C) lacks specific peaks that can be attributed to MDMA, although the overall shape of the signals may still indicate the presence of MDMA, thus enabling chemometric modelling. Contrary, the SCiO (Fig. 4E) seems unsuitable for MDMA detection in ecstasy tablets due to the obscuring effects of the colorants. A noteworthy remark is that multiple NIRone sensors operating at different wavelength ranges exist, from which only the 1550–1950 nm NIRone S2.0 variant was included in this study. Regarding the

forensic application of MDMA detection, it is expected that the 1750–2150 nm NIRone S2.2 sensor will outperform the S2.0 variant because the major 2020 nm peak diagnostic for MDMA will be detectable by this device.

A similar similarity score strategy was followed in order to provide a more quantitative idea of the performance of each NIR spectrometer (Table 3). To test the performance of the NIR spectrometers when the tablets are packed inside a plastic LDPE grip bag, identification of MDMA in intact tablets was also performed. In both experiments, matching was performed with the NIR spectrum of pure MDMA HCl as reference. It must be noted that the plastic packaging will also contribute to the measured spectrum in such a way that spectral features of both MDMA, tablet excipients and LDPE were observed. An earlier study reports on the influence of LDPE packaging showing spectra of the packaging, drugs, and combined [16].

For both the crushed tablets in glass vials and the intact tablets analyzed through a plastic bag, the FP and FN rates clearly reflect the importance of the MDMA-diagnostic spectral features in the ~ 2000 nm and ~ 1500 nm range. Both the ASD and NeoSpectra, capable of detecting the ~ 2000 nm range and the MicroNIR (capable of detecting the ~ 1500 nm range) outperformed the NIRone and SCiO. Especially the SCiO was found unsuitable for MDMA detection in ecstasy tablets. A remarkable result were the three erroneous results for the ASD for tablets in grip bags compared to only 1 FN (i.e. the gray tablet marked with an asterisk in Fig. 4) for the NeoSpectra. A possible explanation is the inclusion of the 1000–1300 nm part of the spectrum (depicted at the left side of Fig. 4A). This wavelength range may still be influenced by electronic excitations of colorants and therefore be less diagnostic for MDMA. Excluding this part of the wavelength range may possibly improve the results, however, individual spectrometer optimization is outside the scope of this study as only the full range spectra were considered.

Summarized, these results furthermore show that NIR sensors that operate in wavelength ranges around 1400–1600 nm or > 2000 nm are preferred for MDMA detection. It must be emphasized that this study only analyzes the fully recorded spectral range of each instrument, and that further optimization by analysis of sub-ranges was not considered. In addition, other parameters that may be important for spectrometer selection such as instrument design, robustness, stability, scan time and

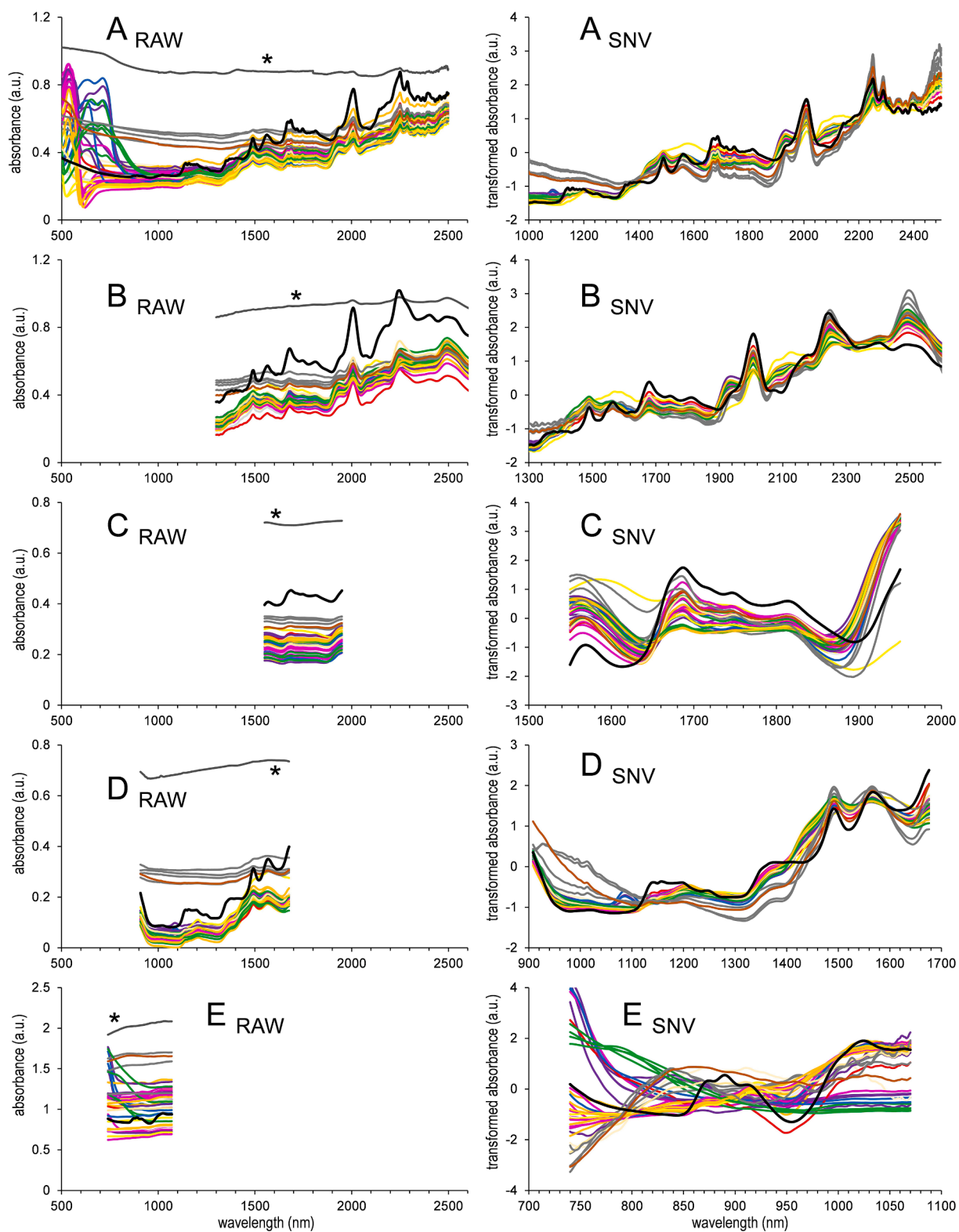


Fig. 4. Effect of colored samples on NIR signal. Crushed MDMA-containing ecstasy tablets analyzed on ASD LabSpec4 (A); NeoSpectra (B); NIRone (C); MicroNIR (D); SCiO (E). Both the raw spectral signal (raw) and preprocessed signal (SNV) are shown. Black line represents MDMA reference spectra. Colors represent the actual color of the ecstasy tablets. Note that the signal from the dark gray ecstasy tablet marked with an asterisk is omitted in SNV for clarity.

Table 3

Performance comparison of the five spectrometers for identification of MDMA in crushed colored tablets in glass vials and intact colored tablets in plastic bags.

	MDMA in ecstasy	ASD	NeoSpectra	NIRone	MicroNIR	SCiO
Crushed tablets in glass vials	Avg Score (Range)	0.91 (0.98–0.61)	0.90 (0.99–0.71)	0.89 (0.99–0.57)	0.87 (0.98–0.43)	0.45 (0.96 - <0.00)
	Decision value	0.60	0.70	0.68	0.60	0.50
	FP (total negatives in set)	0 (32)	0 (32)	5 (32)	0 (32)	3 (32)
	FN (total MDMA in set)	0 (39)	0 (39)	2 (39)	1 (39)	16 (39)
Tablets in plastic bag	Avg Score (Range)	0.27 (0.68 - <0.00)	0.61 (0.90–0.02)	0.40 (0.84 - <0.00)	0.81 (0.98–0.28)	0.60 (0.92 - <0.00)
	Decision value	0.00	0.26	0.01	0.62	0.8
	FP (total negatives in set)	1 (32)	0 (32)	9 (32)	0 (32)	0 (32)
	FN (total MDMA in set)	2 (39)	1 (39)	1 (39)	2 (39)	22 (39)

cost were also not included in the comparison.

Conclusion

The performance characteristics for the detection and identification of illicit drugs of four commercially available portable NIR spectroscopy devices were benchmarked against the high resolution spectra that were recorded by a benchtop laboratory grade VIS-NIR instrument. All portable devices operate at different wavelength ranges and at different spectral resolutions. Individual drug compounds yield NIR spectra with diagnostic peaks at various wavelengths. As a rule of thumb, common drugs-of-abuse yield the most intense and characteristic spectral peaks in the 1500 – 2500 nm NIR range. Less abundant, although still diagnostic peaks were observed in the 1000 – 1500 nm range. Below this range, the spectral peaks become less apparent and can be obscured by interference of strong absorption in the UV-VIS range originating from the sample matrix such as colorants in ecstasy tablets. In the development of NIR-based drugs-of-abuse detectors, smart sensor selection to meet the specific casework challenges is therefore required. For MDMA-detection in colored samples, a sensor capable of detecting the abundant 2020 nm peak specific for MDMA is suggested. Contrary, for relatively pure and white powders such as cocaine and ketamine, multiple sensors may be suitable for use when optimized models and decision thresholds are applied.

Comparisons showed that spectra that were recorded by different instruments are consistent in terms of peak position. On the contrary, the resolution varied significantly among different instruments, which resulted in differences in the captured spectral fine structures. In general, a higher spectral resolution of the sensor is progressively more beneficial in the higher wavelength ranges as the level of detail in NIR signals also increases in this region. This provides interesting leads for further research on spectral databases acquired on full-range (high resolution) benchtop NIR instruments with subsequent calibration transfer or spectral prediction towards various handheld NIR spectrometers. This way, the forensic laboratory can assess the performance of a certain handheld NIR spectrometer *in silico* before investing in the hardware for on-scene detection. Additionally, the optimal wavelength range for a new forensic application can be studied which can aid both hardware development and instrument selection.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Spectral data is available in an accompanying Data in Brief article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.forc.2022.100437>.

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