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Forensic identification of pharmaceuticals via portable X-ray fluorescence and diffuse reflectance spectroscopy

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ABSTRACT

The importance of unknown substance identification in forensic science is vital to implementation or exclusion of criminal charges against an offender. While traditional laboratory measures include the use of gas chromatography/mass spectroscopy, an alternate method has been proposed to efficiently perform presumptive analyses of unknown substances at a crime scene or at airport security points. The use of portable X-ray fluorescence (PXRF) and visible near infrared diffuse reflectance spectroscopy (DRS) to determine elemental composition was applied to pharmaceutical medications ($n = 83$), which were then categorized into 21 classifications based on their active ingredients. Each pharmaceutical was processed by standard laboratory procedures and scanned with both PXRF and DRS. Lastly, the datasets obtained were compared using multivariate statistical analyses. The aforementioned devices indicate that differentiation of unknown substances is clearly demonstrated among the samples with 73.49% DRS classification accuracy. Thus, the approach shows promise for future development as a rapid analytical technique for unknown pharmaceutical substances and/or illicit narcotics.

1. Introduction

Illegal narcotics are prevalent in the United States and worldwide. As federal, state, and local law enforcement agencies struggle to enforce laws, they utilize several scientific methodologies to analyze unknown substances. Importantly, both the type and quantity of illegal substance are considered when establishing the severity of the crime. However, forensic science faces many challenges. Often, criminal offenders are in possession of both legal and illegal substances at the time of offense. When these substances are obtained by law enforcement, they are massed to document the exact amount present in each sample. Forensic toxicologists frequently employ gas chromatography/mass spectrometry (GC/MS) to analytically identify unknown substances. Other traditional analytical methods of drug analysis include use of immunoassays, thin-layer chromatography (TLC), gas chromatography (GC), high-performance liquid chromatography (HPLC), and in more modern labs, Raman spectroscopy or ion mobility mass spectrometry may be utilized. As with any science, modernization accelerates the process of scientific data evaluation.

Regarding the latter, Raman spectroscopy is a newer, state-of-the-art method used among various scientific disciplines including forensic science, and one which has been used to determine the concentrations of street drugs such as cocaine. According to Penido et al. [1], the primary focus of examination via Raman spectroscopy is based on quantification of a suspected drug along with its adulterants and diluents, rather than solely on identification. Ion mobility mass spectrometry is a confirmatory method which separates drug metabolites, and may be used to distinguish complex substances or mixtures, and may be used in the absence of chromatography. Like Raman spectroscopy, it is primarily used for substances which are suspected to have been 'cut' with additional components. Together, these methods might provide valuable information about the origination of a drug based on its manufacturer [1,2].

By contrast, Gahlaut et al. and Hu et al. [3,4] praise the use of liquid chromatography (LC/MS) as a more advanced, versatile, and dependable technique, to be used specifically when substances cannot withstand the high temperatures required for gas chromatography. LC/MS combines physical separation of liquid

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Table 1
Description of pharmaceutical compounds evaluated in the present study sorted by class and brand names.

Class	Brand name	Class name	Chemical formula	Molar mass ($g\,mol^{-1}$)
1	Equate Ready in Case Western Family	Cetirizine HCl	$C_{21}H_{27}Cl_3N_2O_3$	461.80968
2	Equate Western Family XL-3 Claritin	Loratadine	$C_{22}H_{23}ClN_2O_2$	382.88322
3	Top Care Equate	Docusate sodium &Sennosides	$C_{20}H_{37}NaO_7S$ $C_{42}H_{38}O_{20}$	444.55835 862.73912
4	Equate Imodium Quality Plus Walgreens	Loperamide HCl	$C_{29}H_{34}Cl_2N_2O_2$	513.49846
5	Alka-Seltzer Western Family DG Health	Aspirin, Citric Acid, Sodium bicarbonate	$C_9H_8O_4$ $C_6H_8O_7$ $NaHCO_3$	180.15742 192.12352 84.006
6	Ready In Case Western Family Tylenol PM	Acetaminophen, Diphenhydramine HCl	$C_8H_9NO_2$ $C_{17}H_{22}ClNO$	151.16256 291.81568
7	Advil PM Equate Motrin PM	Diphenhydramine citrate	$C_{23}H_{29}NO_8$	447.47826
8	Top Care Walgreens Dramamine	Dimenhydrinate	$C_{24}H_{28}ClN_5O_3$	469.96382
9	Bonine Equate Walgreens Rugby	Meclizine HCl	$C_{25}H_{31}Cl_3N_2O$	481.88544
10	Equate Midol Pamprin Walgreens DC Health	Acetaminophen,Caffeine, Pyrilamine maleate	$C_8H_9NO_2$ $C_8H_{10}N_4O_2$ $C_{21}H_{27}N_3O_5$	151.16256 194.1906 401.45618
11	Goody's Headache Relief Western Family Excedrine Migraine CVS	Acetaminophen, Aspirin, Caffeine	$C_8H_9NO_2$ $C_9H_8O_4$ $C_8H_{10}N_4O_2$	151.16256 180.15742 194.1906
12	Top Care Tylenol Western Family Equate	Acetaminophen	$C_8H_9NO_2$	151.16256
13	Motrin Ready In Case Top Care Western Family Signature Health	Ibuprofen	$C_{13}H_{18}O_2$	206.28082
14	Children's Mucinex Equate Mucus Relief Cough XL-3 Walgreens Family Wellness	Dextromethorphan HBr, Guaifenesin	$C_{18}H_{28}BrNO_2$ $C_{10}H_{14}O_4$	370.32442 198.21576
15	Equate Mucinex DayQuil	Acetaminophen, Dextromethorphan HBr, Guaifenesin, Phenylephrine HCl	$C_8H_9NO_2$ $C_{18}H_{28}BrNO_2$ $C_{10}H_{14}O_4$ $C_9H_{14}ClNO_2$	151.16256 370.32442 198.21576 203.66596
16	Anacin Arthriten Bayer BC Powder	Aspirin, Caffeine	$C_9H_8O_4$ $C_8H_{10}N_4O_2$	180.15742 194.1906
17	Aleve Equate Flanax	Naproxen sodium	$C_{14}H_{13}NaO_3$	252.24099
18	Dr Choice Equate Top Care Tums Western Family	Calcium carbonate	$CaCO_3$	100.0869
19	Quality Product Sudafed Tylenol Walgreens	Acetaminophen, Phenylephrine	$C_8H_9NO_2$ $C_9H_{13}NO_2$	151.16256 167.208
20	Equate Jet Alert	Caffeine	$C_8H_{10}N_4O_2$	194.1906