Quantitative Analysis Of Cocaine Using Fourier Transform Infra Red Spectroscopy-Attenuated Total Reflectance: A Preliminary Investigation

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Abstract

In 2005 of twenty eight representative samples of cocaine taken from material seized by law enforcement officials in Trinidad and Tobago and submitted to the Trinidad and Tobago Forensic Science Centre were quantitatively analyzed using the Centre's standard technique of Gas Chromatography/ Flame Ionization Detection (GC/FID) as well as by Fourier Transform Infrared Spectroscopy/Attenuated Total Reflectance (FTIR/ATR). The both techniques used for the quantization of the cocaine content were statistically compared using the Paired t-test. The results indicated that the methods did not produce significantly different results and hence the FTIR-ATR technique was appropriate for the quantitative analysis of cocaine.

INTRODUCTION

Narcotic and Psychotropic substances are all chemicals that have an effect upon the body and mind. Their use may lead to physical and/or psychological dependence [1]. In scientific publications, narcotics are usually distinguished from psychotropic substances as they are referred to opium alkaloids but for forensic purposes the term "DRUG" can be used to define all of the substances that have a risk of being abused.

The development of plants containing stimulant alkaloids, such as those found in coca and tobacco leaves, occurred 65-250 million years ago. The bitter alkaloids were used as a defense mechanism to ward off dinosaurs, insects and other herbivores. It was not until 5000BC, that humans began using coca leaves for stimulation, nutrition and to control appetite when food was not available [2]. Tobacco, Cannabis, Opium Poppy, Coca bush, Khat and other drug containing plants has been chewed or smoked in many regions of the world as a traditional habit since those times [3].

It was not until 1861; Albert Niemann isolated cocaine from other chemicals in the Coca Leaf. This earned him his PhD at the University of Gottingen in Germany where his work was based. Since the extract was 200 times more potent than the coca leaf itself the stage was set for the widespread use and abuse of cocaine. This occurred 20 years later due in part to Karl Koller who discovered the anesthetic properties

and Sigmund Freud who published Uber Coca. Their writings and other papers promoted the use of the refined cocaine for a variety of ailments including depression, gastric disorders, asthma, and morphine or alcohol addiction. Its use as local anesthetic or as an aphrodisiac was also suggested [4]

In 1914 cocaine was banned in the U.S. under the Harrison Act, which controlled the sale of opium, opium derivatives and cocaine [5]. Cocaine increases alertness, wakefulness, elevates the mood, induces a high degree of euphoria, decreases fatigue, improves thinking, and increases concentration and energy. In large doses, users often display symptoms of Psychosis with confused and disorganized behavior, irritability, fear and paranoia. Cocaine is a highly addictive substance developing a strong tolerance and psychological dependence and moderate physical dependence. Illicit Cocaine is usually distributed as a white crystalline powder in hydrochloride salt form or as an off white chunky material which is cocaine free base and commonly named as crack. Cocaine powder is often diluted with sugars and local anesthetics like lidocaine [5,6,7].

There are so many articles in the literature regarding the quantitative and qualitative analysis of drugs. Thin Layer Chromatography, Infra Red Spectroscopy and Gas Chromatography are commonly used for qualitative analysis and Gas Chromatography and High Pressure Liquid

Chromatography for quantification. Due to the clandestine development of new drugs and the ever increasing number of samples to be analyzed by forensic laboratories, the scientist is required to employ powerful hyphenated and fast techniques like LC-MS, LC-MSMS, GC-FTIR and Capillary Electrophoresis. Chromatographic methods have several disadvantages as not only are they relatively time consuming and expensive they also require specific extraction methods and the technique is usually limited with the solubility of target compounds. At the Trinidad and Tobago Forensic Science Centre the GC/FID technique is routinely used for the quantitative analysis of cocaine in seized material.

Work done by Levy et al. (1996) studied illicit heroin samples by FTIR with KBr pellet technique. [8]. Other researchers have utilized near-IR and Raman Spectroscopy to analyze illegal drugs [9,10,11]. Koulis et al. (2000) collected spectra of 455 controlled and non-controlled drug standards with FTIR–ATR technique and they constituted a spectral library [12].

In this study, the advances of FTIR technique with particular emphasis on the use of the ATR technique have been exploited for the quantization of cocaine as for being a fast method and requiring almost no preparation work.

The cocaine content in twenty eight (28) representative samples will be quantitated using a proposed FTIR/ATR technique and the conventional GC/FID technique. The results obtained by both methods would be s statistically compared to determine whether the FTIR/ATR technique is a viable alternative for the quantitative analysis of cocaine.

MATERIALS AND METHODS

Twenty eight (28) samples seized materials were randomly selected in 2005. These samples were seized from different parts of Trinidad and Tobago by Police Officers and submitted to the Trinidad and Tobago Forensic Science Centre for analysis. The samples were analyzed using two analytical techniques: FTIR/ATR and GC/FID.

FTIR/ATR

The 3 standards used to generate the calibration curve was 100%, 50% and 25% cocaine HCl (Lipomed AG, Switzerland). For each standard, a minute amount was placed unto the ATR crystal (ZnSe), of a Nicolet Avatar FTIR Spectrometer. A pressure of 8psi was applied to the crystal and the spectrum taken. The absorbance values for the major peaks in cocaine HCl were recorded from the ATR spectrum. Each standard was measured 3 times and an average taken to generate the calibration curve. Calibration curves for each cocaine HCl standard were plotted for all the characteristic peaks. The wavelength giving the best fit calibration curve was chosen to be compared with the samples. The samples were similarly analyzed and the concentration of cocaine in the seized material determined from the calibration curve.

GC/FID

The samples were analyzed using the Internal Standard method currently employed as the Standard Operating Procedure at the Trinidad and Tobago Forensic Science Centre.

Standard solutions of a concentrations of 10mg/mL, 5mg/mL and 2.5mg/mL of Cocaine HCl in 0.5mg/mL Tetracosane (methanol/chloroform solvent mixture (1:1)) were prepared. Approximately 100mg of illicit cocaine sample was weighed out into a 10ml volumetric flask and dissolved in 0.5mg/mL Tetracosane (methanol/chloroform solvent mixture (1:1). The standards and samples were analyzed using the GC/FID.

Gas Chromatograph Operating Conditions:

Detector: F.I.D. (hydrogen at 30ml/min, air at 450 ml/min)
Column: HP5 (cross-linked 5% phenyl methyl siloxane)
Carrier gas: Helium, 2ml/min.
Injection mode: Split; ratio 60:1
Injection temperature: 260 ° C.
Oven temperature: 250 ° C.
Detector temperature: 280 ° C.
Volume injected: 1μl.
Internal Standard:tetracosane

STATISTICAL ANALYSIS
THE PAIRED T- TEST []

In this project, two methods of analysis are compared by studying test samples containing different amounts of Cocaine. There can be variation in the measurements due to random measurement errors and differences in the method itself. The Paired t-test determines if there is a significant difference in results due to the method.

$$t_{(calculated)} = D / (S / \sqrt{n})$$

Di = difference between each pair of results for each sample.

D = Average of Di.

S = Standard deviation. $= \sqrt{\sum (D_i - D)^2 / n-1}$

If t $_{(calculated)}$ is greater than t $_{(tabulated)}$, then there is a significant difference in results. If

t $_{(calculated)}$ is less than t $_{(tabulated)}$, then there is no significant difference in results.

RESULTS AND DISCUSSION

The cocaine hydrochloride standards were analyzed using the FTIR/ATR technique and the absorption peaks corresponding to the characteristic functional groups in the cocaine molecule were observed (see Figure 1). Calibration curves were plotted for each of the characteristic absorption peaks and the frequency giving the best fit calibration curve was found to be 732 cm $^{-1}$. The calibration at this frequency was used to quantify the cocaine samples using this technique. The samples were then analyzed using the GC/FID technique. The results of the analysis of the cocaine samples using both techniques are shown in Figure 2.
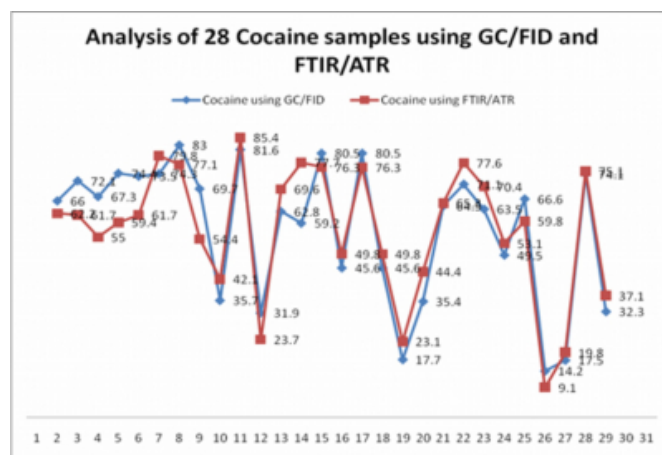
Figure 1

Figure 1: showing the characteristic Infra-red functional groups on the Cocaine molecule
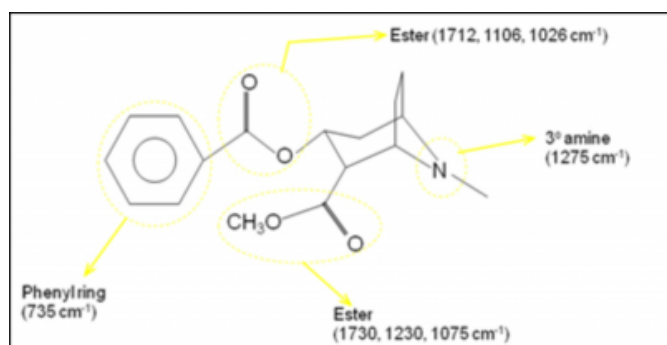
Figure 2

Figure 2: showing the results of the analysis of the cocaine samples using both FTIR/ATR and GC/FID

The both techniques used for the quantization of the cocaine content in the 28 samples were statistically compared using the Paired t-test. The value of t $_{(calculated)}$ = 0.6695 and the p-value obtained was 0.5 and t$_{(tabulated)}$ = 2.0518 [value obtained from the t-distribution tables at a 95% confidence level and a degree of freedom of n-1 which is equal to 27]. Since t $_{(calculated)}$ was less than t$_{(tabulated)}$, one can conclude that the methods did not produce significantly different results.

CONCLUSION

The results indicated that there was no difference between the GC/FID and the FTIR/ATR techniques for the quantization of cocaine in the illicit samples. Unlike conventional Chromatographic techniques and Infrared methods using KBr and Nujol mull techniques, working with ATR requires no complicated sample preparation and this makes the technique very advantageous for the identification and quantization of cocaine. This technique can be used as an alternative to GC/FID. As future aspects of the study, the number of illicit samples should be increased and the influence of different compositions of adulterants and additives should be performed. The applicability of the FTIR/ATR technique for the identification of other types of drugs should be attempted.

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