ISSN 2348-1218 (print)
International Journal of Interdisciplinary Research and Innovations ISSN 2348-1226 (online)
Vol. 2, Issue 3, pp: (56-64), Month: July 2014 - September 2014, Available at: www.researchpublish.com

Detection and Identification of 3, 4-Methylenedioxymethcathinone (Methylone) As an Illicit Drug Using GC-MS, LC-(TOF)-MS, ATR-FTIR and FT-Raman in the Forensic Science Laboratory in South Africa

[1]ZA Mangombo, [2]PM Mthembi, [3]AK Maleke, [4]PM Modise

[1,2,3,4] Forensic Science Laboratories, Chemistry Section, 47 Silverboom Avenue, Plattekloof 7506, South Africa

Abstract: **3, 4-Methylenedioxymethcathinone (MDMC), known as methylone, is a new analog of methcathinone, which is found also in the group of central nervous system stimulant. Street samples consisting of capsules seized by the South African Police were submitted to the Forensic Science Laboratory (FSL) for further analysis. In order to detect these samples, the following techniques such as Gas chromatography-mass spectrometry (GC-MS), Liquid chromatography coupled with (time-of-flight) mass spectrometry (LC-(TOF)-MS), Attenuated total reflectance-Fourier transform infrared spectrometry (ATR-FTIR) and Fourier transform Raman (FT-Raman) were used to identify the seized materials. The study of the mass spectra of the samples and its acetyl derivative were indication of positive Methylone (3,4-Methylenedioxymethcathinone). The literature survey was used as a reference material.**

Keywords: **Methylone, GC-MS, LC-(TOF)-MS, ATR-FTIR, FT-Raman, Forensic Science, Laboratory (FSL).**

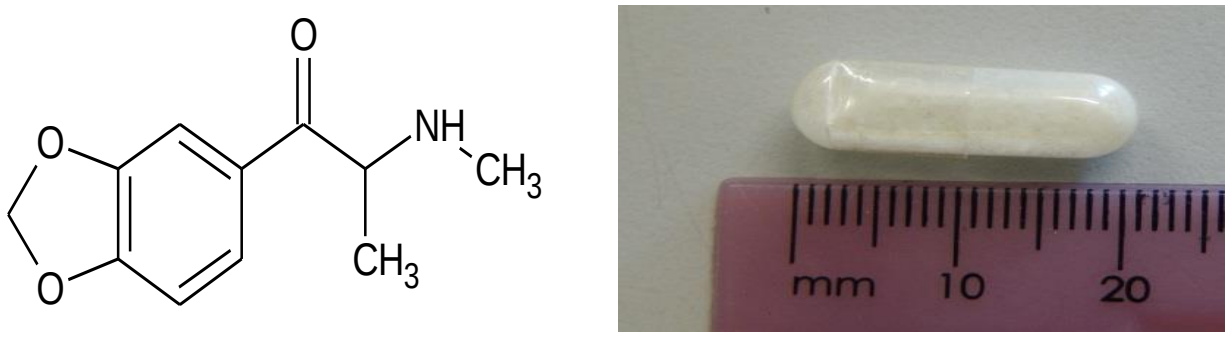
I. INTRODUCTION

Drug abuse is currently a worldwide problematic affecting developed and developing countries including South Africa. Nowadays no nation is free from this risk. This has engaged more pressures on national laboratories as to not only identify seized materials but also to detect drug abuse, new designer drug and its analogs. Analog compounds are defined as compounds with similar electronic structures but different atoms or structural derivatives of a parent compound. Mephedrone (4-methylmethcathinone),1-(1,3-benzodioxol-5-yl)-2-(methylamino) butan-1-one (bk-MBDB) and methylone (3,4-Methylenedioxymethcathinone) are all methcathinone analogs [1]. Methcathinone known as ephedrone, is a central nervous stimulant (CNS) found in leaves of the khat bush (Catha edulis). Methcathinone is strictly under the Controlled Drugs and Substances Act of the Drugs and Drug Trafficking Act in South Africa since 1992.

The expertise of Forensic Science Laboratory (FSL) to detect and identify unknown compounds is extremely significant since new, non-controlled designer drugs are appearing on the market with increasing level. However, the analysis of analogs drugs presents a challenge for Forensic analyst to identify the new designer drugs because the reference material and literature reviews are not readily available. Reference materials have always been an issue when new substances are encountered. Yet, this makes very difficult to identify the compounds of interest for the methcathinone analogs. Designer drugs have similar chemical structures and physiological effects to illicit drugs. Unfortunately, consumers have little to no knowledge of the long-term toxicity or immediate physiological effects that are associated with these new designer drugs, because they are not necessarily associated with the original illicit drug that was replicated. The truth is that societies have found methods to consume these products for their hallucinogenic moves.

As a part of our research which is based on the new designer drugs in the market, after the analysis of the unknown exhibit material in the laboratory, the study of the mass spectra of the sample and its acetyl derivative has shown that the structure of the compounds was identified as methylone (3,4-Methylenedioxymethcathinone). The literature survey was used as reference material [2], [3], [4], [5]. This is the first time that methylone has been shown to be in the market circulation, even though numerous reports have described its analytical methods [2].

Some study has shown that methylone (Fig.1)with other two compounds such as MDPV (3,4-methylenedioxypyrovalerone) and mephedrone (4-methylmethcathinone) are three examples of research chemicals that hidden under the common word bath salts that have no reports use for moderation in baths, however instead contain powerful chemical stimulants comparable in effect to cocaine and methamphetamine [6], [7]. None of these chemicals are currently scheduled under the Medicines and Related Substances Control Act (1965) and/or the Drugs and Drug Trafficking Act (1992) in South Africa. This is possible to occur in the near future and subsequently these chemicals may be scheduled.



(a) (b)

Fig.1. (a) Chemical structure of the methylone (3, 4-Methylenedioxymethcathinone) and (b) Picture of the methylone capsule received in Forensic Science Laboratory.

However, law enforcement cases involving synthetic cathinones and its derivatives [8], [9], [10], [11] can be prosecuted under the Controlled Substances Analogs in the Medicines and Related Substances Control Act and/or Drugs and Drug Trafficking Act if the synthetic cathinone meets the definition of a controlled substance analog. Methylone is psychoactive chemical that is structurally and pharmacologically similar to the hallucinogenic stimulant substance 3,4-methylene-dioxymethamphetamine (MDMA). Methylone was used for the purpose as to an anti-depressant drug. Methylone including with mephedrone and MDPV are generally popular with the youth in urban environments [10]. These substances are manufactured in the form of powders, capsules and tablets. They are abused by consumers under the age of 25 and are frequently associated with other club drugs such as cocaine, amphetamine, MDMA and methcathinone. The most common routes of administration are inhalation by snorting the powder and injection by taking capsules or tablets. The powder can also be injected or swallowed. Consumers report effects occurring a few minutes to 15 minutes after administration, depending on the route of administration, and the effects can last up to 3 hours. Hence, it is imperative to identify and to gather information of these substances to establish prevalence and trends to adverse health effects is of particular interest on the pharmacology, toxicity and abuse of synthetic cathinones and products containing these substances to support possible scheduling of methylone and other substances such as mephedrone and MDPV [10].

These new designer drugs have created a complex matrix of new chemicals in the market. Lack of reference material, literature reviews, mass spectral data and proper classification of the chemicals has been challenged and more complicated for scientist to overcome the situation of their identification. Methylone has not yet been reported for its physico-chemical data; therefore, it required structural explanation and synthesis of a reference compound to explicitly determine its identity. Only its analytical studies have been reported by Maheux*et al* [2]. A literature review for the study of methylone and other relative compounds has been published with chromatographic and spectroscopic data for analytical methods for the characterization of three methcathinone analogs including sample preparation techniques and validation data [2], [12], [13]. To confirm the structure of the methylone, the following techniques such as Gas chromatography-mass spectrometry (GC-MS) [14], Liquid chromatography-time of flight mass spectrometry (LC-(TOF)-MS) [15], Attenuated total reflectance-Fourier transform infrared spectrometry (ATR-FTIR) [16] and Fourier transform Raman (FT-Raman) [17] were used to identify the new unknown.

II. EXPERIMENTAL

A. Materials and chemicals

Ten (10) capsules of unknown compounds were from the Western Cape Forensic Science Laboratory and were submitted to the Pretoria Forensic Science Laboratory for further analysis. Acetic anhydride (AA) was used as a derivative agent for GC-MS analysis. N-acetyl derivative of the sample was prepared by adding 1 drop of AA to 1 mL of chloroform (99.0%) containing an appropriate amount of unknown compound and sample solution was further used for GC-MS analysis. All chemicals and solvents used without further purification were of reagent grade and were all purchased from Merck South Africa (www.merck.co.za). All reagents used were of analytical grade or enhanced quality.

B. Instrumentation and sample analysis methods

GC-MS analysis

GC-MS analysis was carried out using an Agilent Technologies system (Chemetrix, RSA) consisting of gas chromatograph (GC), Agilent 7890A, and mass selective (MS) detector (Agilent 5975 C VL MSD) with an auto sampler 7683 B series (1 µL injection). The instrument is controlled by a data system that consists of a HP Compaq computer. Chromatographic separation was performed on a computer controlled auto sampler used with a fused-silica capillary column HP-5MS (30 m x 0.25 mm x 0.25 µm; film thickness 0.25 µm; J&W Scientific, Folsom, CA, USA). The injector was used splitless mode at 250^0C. The gas chromatograph (GC) oven temperature was consisted of an initial temperature of 38^0C for 1min, raised to 110^0C at rate of 10^0C/min, and then raised to reach 300^0C at 15^0C/min. This temperature was maintained for 5 min. High-purity helium (99.9995%) was used as the carrier gas, at flow rate of 1 mL/min. The detector (MS) parameters used was performed as follows: the interface temperature (280^0C), the inlet temperature (250^0C), the ion-source temperature (230^0C), the ionization mode, the electron ionization (EI), the ionization voltage or energy (70 eV) and the mass spectrometer (quadrupole) used in scan mode. The spectra were recorded in the scan range of mass particles (m/z) from 40 to 550 amu, at scan time of 1 scan/sec (scan rate).

For GC-MS sample preparation, an amount of unknown sample was dissolved in one (1) drop (0.5 ml) of 1% ammonia (NH_3) *aq*. in the Durham tube followed by the addition of 1.0 mL of chloroform (99.0%). From the upper layer of the organic solution (analyte), one (1) drop of this analyte was transformed into a vial containing 2.0 mL of chloroform (99.0%). An addition of 1 drop of an acetic anhydride (AA) to the aliquot solution was then used as a derivative agent in the solution. The aliquot of the sample was further used for GC-MS analysis.

LC-(TOF)-MS analysis

LC-(TOF)-MS analysis was carried out using an Agilent Technologies (Waldbronn, Germany) 1100 series instrument, comprising a vacuum degasser, auto sampler, binary pump, and column oven. The system of chromatographic separation was performed with a Phenomenex (Torrance, CA, USA) Luna C-18(2) 100 x 2 mm (3 µm) column and a 4 x 2 mm precolumn in gradient mode at 40^0C with a flow rate of 0.3 ml/min. The mobile phase components used for introducing samples to the trap column were 5 mM ammonium acetate (0.5ml/min) in 0.1% formic acid (10 mM)-acetonitrile: 95:5, v/v at flow rate of 0.2 mL/min. The proportion of acetonitrile was increased from 10% to 40% in 10 min, to 75% in 13,50 min, to 80% in 16 min, and held at 80% for 5 min. Equilibrium time was 6 min and injection volume was 10 µL. Both LC separation and ion-line extraction were carried out at 30^0C. Quantitative analysis was carried out in triplicate in the selected-ion monitoring (SIM) mode including the other operating parameters such as nebulizer nitrogen gas at flow-rate of 1.5 L/min; curved desolvation line (CDL) voltage (25 V); Q-array bias (10 V); CDL temperature (250^0C); and ion-source temperature (200^0C).

ATR-FTIR analysis

ATR-FTIR analysis was performed using a Bruker Vector 22 mid-IR spectrometer with a single reflection diamond ATR accessory. ATR crystal (50 mm x 10 mm x 2mm, 45^o), in which IR beam can reflect about 25 times, was made of single crystalline silicon. The detector was used at the resolution of 4 cm^{-1} with 1024 scans. The ATR-FTIR spectra region was recorded in the range between 4000 cm^{-1} and 500 cm^{-1}.

ISSN 2348-1218 (print)
International Journal of Interdisciplinary Research and Innovations ISSN 2348-1226 (online)
Vol. 2, Issue 3, pp: (56-64), Month: July 2014 - September 2014, Available at: www.researchpublish.com

FT-Raman analysis

FT-Raman measurements were carried out by using a PerkinElmerspectrometer (PerkinElmer, USA) with the Raman Model R Photoelectric recording Raman spectrometer. The excitation source in the FT-Raman instrument was a laser operating by emitting continuous radiation at wavelength of 1064 nm with a maximum power of 1.5 W at the sample. This condition is very significant in forensic science in regard with drug analysis, since shorter wavelength lasers operating throughout the visible region to around 785 nm often excite shattering levels of fluorescence from most street-quality samples, making the collection of Raman data difficult or impossible. The system was equipped with the installed detector in the laser Raman module such as InGaAs (Indium-Gallium Arsenide), which is an air cooler detector. No special sample preparation was needed in the experiment. The sample was put in NMR tube sample holder. The used sample configuration was 180^{o} reflective optics with a fully motorized sample position adjustment feature. A laser output power of 0.77 W was used, which was low enough to prevent possible laser-induced sample damage yet provided a high signal-to-noise ratio. Data were collected at 16 cm^{-1} resolution with 256 scans. The entire laser Raman spectra were collected in the shift spectral range between 4000 and 100 cm^{-1}. The system was operated with the OMNIC 5.1 software and experiments were done in duplicate.

III. RESULTS AND DISCUSSION

Gas chromatography-mass spectrometry (GC-MS) and Liquid chromatography-time of flight mass spectrometry (LC-(TOF)-MS)

Both techniques GC-MSand LC-(TOF)-MS offer evidence on molecular weight and partial structure, respectively. Hence analysis of the sample using both techniques should enable clarification of the structure without the standard. The molecular ions ($[M]^{+}$) were observed as base peak ions for the capsule sample analysed using both techniques in this study (Fig. 2 and Table 1).

The GC-MS data collected for the capsule sample (as unknown sample) is shown in Figure 2. The present result has shown that the molecular ion for the unknown sample was either weak or absent and can be seen only after computer enhancement (Fig. 2). Therefore, the unknown sample was further analysed with acetic anhydride (AA). Adding the acetic anhydride (AA) to the sample extraction, consequently an acetyl group is added to the nitrogen atom to obtain the N-acetyl derivative. This addition of a functional group reduces the susceptibility of the nitrogen atom to active sites in the system enormously, resulting in sharp, symmetrical chromatographic peaks using GC-MS technique (Fig. 3). The GC-MS data for the N-acetyl derivative of the unknown sampleshowed a similar fragmentation pattern as compared with the GC-MS data reported previously in literature [2].

The spectrum data has shown the presence of the molecular ion of *m/z* 249 (Figure 3). This indicates that the molecular ion is 207 since M + 42 is equal to 249. The α-cleavage (M-15) fragments were found at *m/z* 192 and 234 at low intensities for the capsule sample and its N-acetyl derivative respectively.

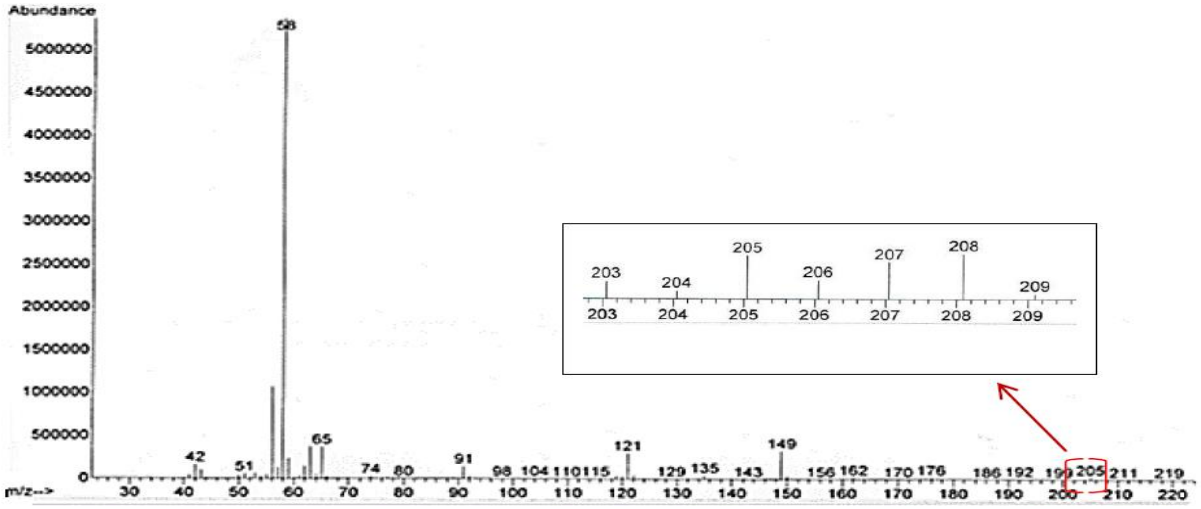


Fig. 2. GC-MS spectrum of the non-acetylated capsule sample

ISSN 2348-1218 (print)
International Journal of Interdisciplinary Research and Innovations ISSN 2348-1226 (online)
Vol. 2, Issue 3, pp: (56-64), Month: July 2014 - September 2014, Available at: www.researchpublish.com

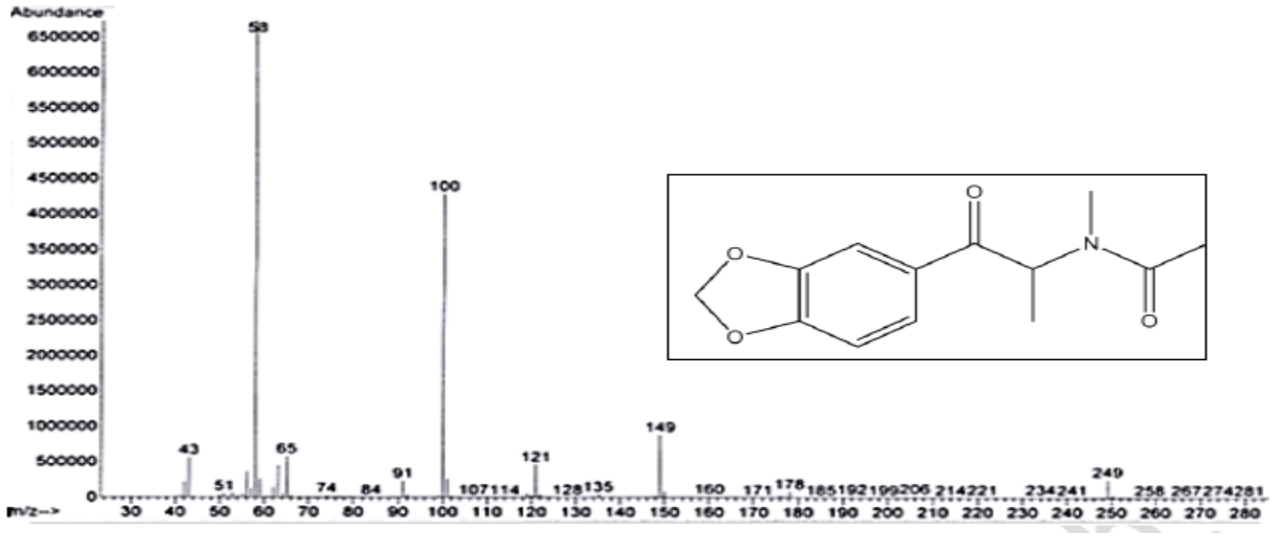


Fig. 3. GC-MS spectrum of the acetylated capsule sample

The base peaks for the capsule sample and its acetyl derivative, respectively at *m/z* 58, relates to the formation of an iminium ion ($C_3H_8N^+$) and is similarly characteristic of methcathinone. The peak for the acetyl derivative of the capsule sample, at *m/z* 100, corresponds to the formation of an iminium ion ($C_5H_{10}NO^+$) and is an indication of characteristic of methcathinone. Hence, the ions at *m/z* 149 and *m/z* 121 for the capsule sample and its acetyl derivative are consistent with the methylenedioxybenzoylcation, obtained by consequent loss of iminium ion, and methylenedioxyphenylcation (obtained by loss of CO) reported for 3,4-Methylenedioxymethcathinone (methylone).

In addition, further analysis of the capsule samples using LC-(TOF)-MS methods was studied. The sensitivity and the selectivity of LC-(TOF)-MS depend on the resolving power of the instrument, which is based on the *m/z axis*. The higher the resolution can provide by the instrument, the better the selectivity for explicit identification of the compounds, which is an indication of better sensitivity of the instrument. The sampling technique has overcome initial limitations leading to instruments capable to perform both quantitative and qualitative analysis. The time of flight mass, (TOF)-MS, instruments are capable of range between 5,000-10,000 resolving power expressed in terms of full peak width at one–half maximum (FWHM) [18].

TOF-MS has a high acquisition speed include high selectivity and high accurate mass measurement (yield mass accuracy < 2 ppm) as a result of an adequate calibration range as well as full scan spectral sensitivity. The accuracy TOF-MS, mass analysers, is much higher than any other instrument due to the excellent ion separation and detection in the flight tube. Accurate mass spectra achieve a much better identification and detection of target compounds for the estimation of complex matrices. In addition, the accurate mass measurement gives the elemental composition of parent and fragment ions (Figure 4), used to identify unknown species and greater differentiation of isobaric species (two different compounds with the same nominal mass but different elemental composition, and thus, different exact masses).

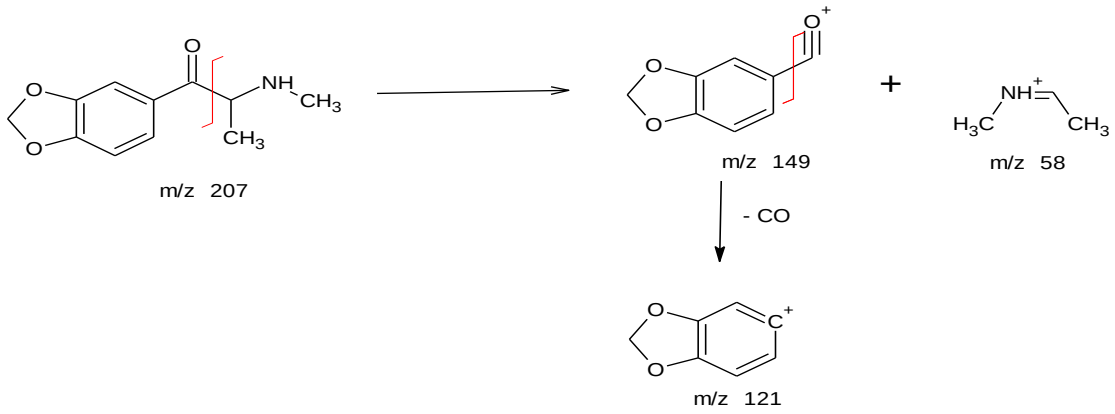


Fig. 4. Fragmentation pattern of the methylone spectrum

High resolving power of a time of flight instrument can discriminate between isobaric interferences within 0.05 Da mass differences [18]. The use of LC-(TOF)-MS allows an improved selective mass measurement of a target compound fragment ions (Figure 4), thus eluding the problem of sample interferences. When a wide window is selected in the extracted ion chromatogram, hence, interferences might be present; and when the same window is narrowed, a more selective identification of the target compounds can be achieved and an enhanced signal-to-noise for the preference compounds. However, the selectivity can be improved by decreasing mass window as this resulting in an almost complete loss of the interferences from the isobaric contaminant ions. Therefore, the acquisition of the full product ion spectra at accurate mass can allow the explicit confirmation of the compounds detected.

The molecular ion of the capsule sample was confirmed with LC-(TOF)-MS as shown in table 1 below. The table has shown the mass errors obtained for the parent ion and the selected product ions of the target compound. The data shows a score of 81% and a mass error of 2.87 ppm for the molecular ion of 207, which has given a high confidence in the identification and detection of the methylone compound.

Table 1. LC-(TOF)-MS data of the capsule sample

Calculated mass (m/z)	*Measured mass (m/z)*	*Difference (ppm)*	*Abundance*	*Formula*	*Molecular ion*
207.09	207.0889	2.87	_	$C_{11}H_{13}NO_3$	$[M]^+$
208.0968	208.0962	-2.91	19552	$C_{11}H_{14}NO_3$	$[M + H]^+$
209.1	209.1073	17.6	2661	$C_{11}H_{14}NO_3$	$[M + 2H]^+$
210.1022	210.1073	24.19	254	$C_{11}H_{14}NO_3$	$[M + 3H]^+$

Attenuated total reflectance-Fourier transforms infrared spectrometry (ATR-FTIR) and Fourier transform Raman (FT-Raman) spectroscopy

Attenuated total reflectance-Fourier transform infrared spectrometry (ATR-FTIR) has generally been used widely for the identification of the compounds in the field of Forensic Science. Yet, Fourier transform Raman (FT-Raman) spectroscopy has been used in numerous areas primarily for its capacity to fast detect various kinds of compounds without complicated pre-treatment. In addition to its advantages such as no sample preparation, non-destructive analysis, capacity to sample through glass or thin plastic containers and capability to study aqueous solutions as water has merely a weak Raman spectrum. Both analytical techniques are become very attractive for the Forensic Science environment. Figures 5 and 6 shows, respectively, the ATR-FTIR spectrum and Raman spectra of the capsule samples, which further were identified as methylone compounds and were compared consistent with the ATR-FTIR and FT-Raman spectra previously recorded in literature [2]. Although infrared (IR) spectroscopy has conventionally assisted as a significant method for selection and identification of the unknown compounds, however, Raman spectroscopic data has appeared as a powerful technique in the field of Forensic laboratory.

Raman spectroscopy is a non-destructive technique which, like IR, offers a "fingerprint" spectrum of chemical compounds. In numerous cases, bands which are weak or totally inactive in IR tend to be strong in Raman and vice-versa. Consequently, both techniques are balancing and can deliver a more comprehensive characterization of the target compounds.

The ATR-FTIR spectrum of the capsule sample shown in Figure 5 explains that besides some alkyl C-H and aryl C-H absorption bands at about 2800-3000 cm^{-1}, hence, strong C=O absorption is detected at 1676 cm^{-1} and also the dominant C-O absorption is detected at 1250 cm^{-1}. On the other hand, some absorption bands were also detected at 1028, 1450 and 1650 cm^{-1}, which were assigned to the substituted-aromatic ring breathing vibration mode, CH_2 absorption and N-H absorption bands, respectively. Low intensity of the absorption band at 1380 cm^{-1} (assigned to methyl group – CH_3) is due to much stronger CH_2 absorption band at 1450 cm^{-1} can be easily seen. The analytical technique applied in this study has shown an indication of the confirmation of the structure for methylone compound.

ISSN 2348-1218 (print)
International Journal of Interdisciplinary Research and Innovations ISSN 2348-1226 (online)
Vol. 2, Issue 3, pp: (56-64), Month: July 2014 - September 2014, Available at: www.researchpublish.com

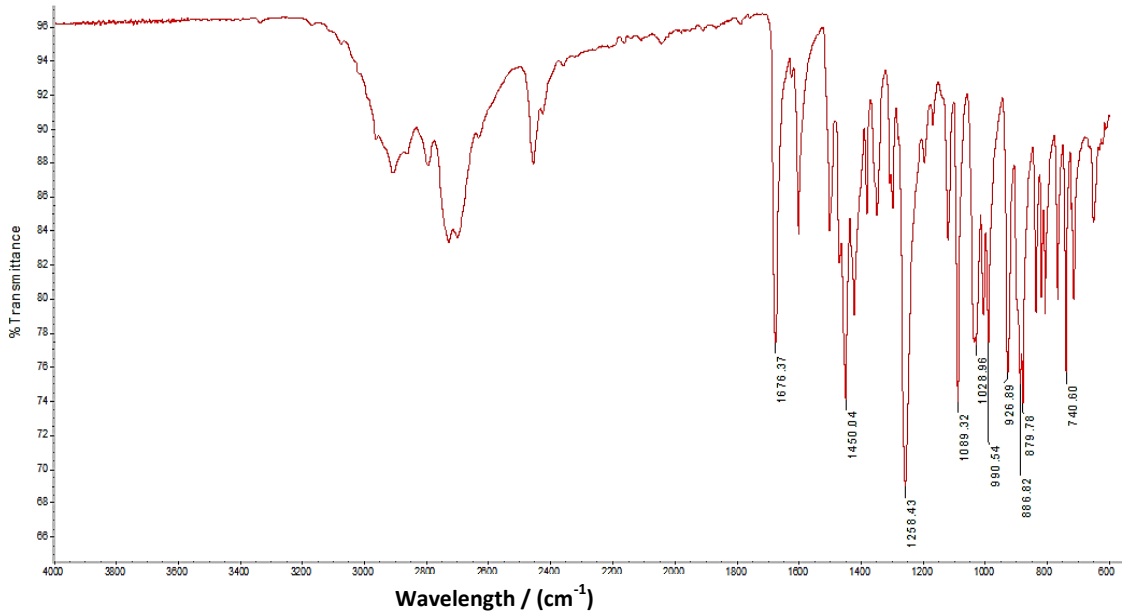


Fig. 5. ATR-FTIR spectrum of the capsule sample

Fig. 6 shows the FT-Raman spectrum of the capsule sample, which the spectra were pretreated by restricting the spectral region from 3200 to 100 cm^{-1} and setting the baseline intensity to zero and the most intense peak to one. The result (Figure 6) is shown the measurement of the capsule sample used as an unknown and subsequently was compared to the literature [2], which the sample was reported as methylone. The FT-Raman spectrum of the capsule sample was measured under the conditions described above. It can be observed a strong and sharp Raman peak at around 1676 cm^{-1} and other different peaks detected. Several Raman peaks are observed in the spectrum of the capsule sample (known as methylone), mainly located at 1028 cm^{-1} (substituted-aromatic ring stretch), 1250 cm^{-1} (C-O stretch), 1380 cm^{-1} (CH_3 stretch), 1450 cm^{-1} (CH_2 stretch), 1650 cm^{-1} (N-H stretch) and 1676 cm^{-1} (C=O stretch). Thus it is suggested that FT-Raman analysis is also confirmed the detection of methylone.

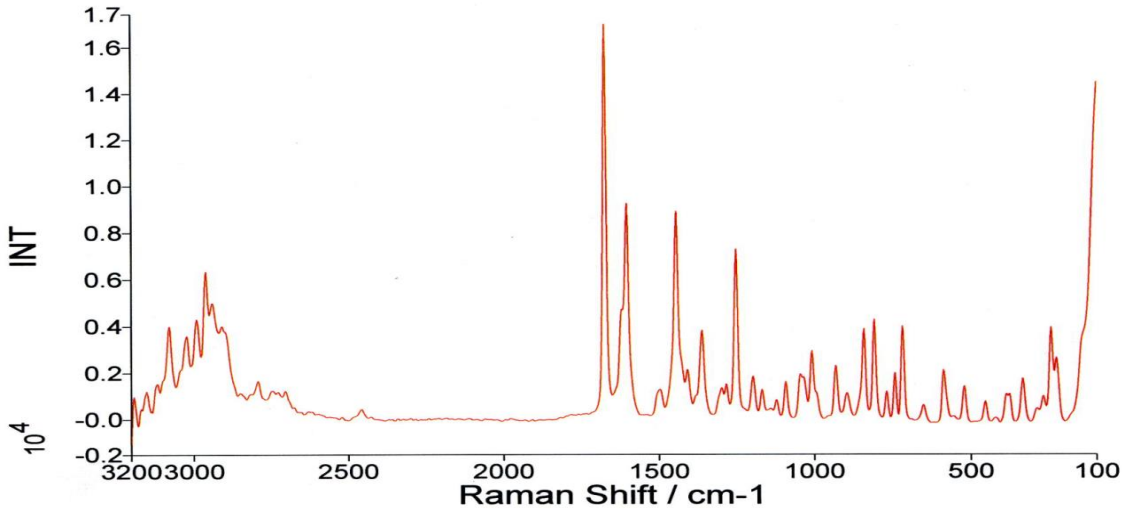


Fig. 6. FT-Raman spectrum of the capsule sample

When comparing the FT-IR and FT-Raman spectroscopy data for the methylone compound, as expected, many of the peaks observed on the FT-IR were similar also in the FT-Raman spectra (Figs 5 and 6). Both analytical techniques have shown the effectiveness for detection and identification of methylone.

IV. CONCLUSIONS

The capsule samples submitted in our Forensic Science Laboratory (FSL) in Pretoria were identified to contain methylone and were corresponded with the data previously study in the literature [2]. The results indicate that it is possible to detect and identify methylone using different analytical techniques such as GC-MS, LC-(TOF)-MS, ATR-FTIR and FT-Raman. The literature survey was used as a reference material. The applicability of these methods to the detection and identification of methylone has been successfully demonstrated on casework samples. The techniques studies in this paper are suitable methods and have the potential to become powerful methods for the easy and rapid for the detection and identification of the new non-controlled designer drugs. For these increasing drugs load of many Forensic Laboratories, these techniques can be applied to identify the unknown exhibit material. FT-Raman provides quick non-destructive and easy sample screening. The more complex GC-MS need only be used when a more in-depth analysis is required.

ACKNOWLEDGMENTS

The authors are thankful for the support of the management of Forensic Science Laboratory (FSL) component, the management of Quality component and the Divisional Commissioner of Forensic Services as a whole.

REFERENCES

[1] Deruiter J, Hayes L, Valaer A, Clark CR, Noggle F.T. Methcathinone and Designer Analogs-Synthesis, Stereo chemical Analysis, and Analytical Properties. J ChromatogrSci 1994, 32, 552, 64.

[2] Maheux C R, Copeland C R and Pollard M M.Characterization of Three Methcathinone Analogues: 4- Methyl methcathinone, Methylone, and bk-MBDB.Microgram Journal 2010; 7(2); 42-49.

[3] Camilleri A, Johnston MR, Brennan M, Davis S, Caldicott DGE. Chemical analysis of four capsules containing the controlled substance analogues 4-methylmeth-cathinone, 2-fluoromethamphetamine, α-phthalimidopropiophenone and N-ethyl-cathinone. Forensic SciInt 2010; 197(1-3):59-66.

[4] Westphal F, Junge T, Rosner P, Sonnichsen F, Schuster F. Mass and NMRspectroscopic characterization of 3,4-methylenedioxypyrovalerone: a designer drugwith-pyrrolidinophenone structure. Forensic SciInt 2009;190(1-3):1-8.

[5] Dal Cason TA. The characterization of some 3,4-methylenedioxycathinone(MDCATH) homologs. Forensic SciInt 1997;87(1):9-53.

[6] Isenschmid D.S, Levine B.S and Caplan Y.H. A comprehensive study of the stability of cocaine and its metabolites. J. Anal. Toxicol. 1989, 13, 250-256.

[7] Hornbeck C.L and Czarny R.J. Quantification of methamphetamine andamphetamine in urine by capillary GC/MS. Part 1.Advantages of trichloroacetylderivatisation. J. Anal. Toxicol. 1989, 13, 251-262.

[8] Award T.C.R, Clark C.R, De Ruiter J. Chromatographic and mass spectral studies onmethoxymethcathinone related to 2, 3-methylenedioxymethamphetamine.J. Chromatogr. Sci. 2006, 44 (3), 155-161.

[9] Archer R.P. Fluoromethcathinone, a new substance of abuse. Forensic Sci. Int.2009, 185, 1-8.

[10] Gibbons S, Zloh M. An analysis of the 'legal high' Mephedrone.Bioorg.Med,Chem. Lett. 2011, 20, 4135-4139.

[11] Brand S.D, Freeman S, Sumnall H.R, Measham F, Cole J. Analysis of NRG 'legalhighs' in the UK: identification and formation of novel cathinones. Drug Test.Anal. 2010, 10.1002/dta.204.

[12] Toole K.E, Fu S, Shimmon R.G, Kraymen N. Color Tests for the preliminary Identification of Methcathinone and Analogues of Methcathinone. MicrogramJournal 2010, 9 (1), 27-32.

[13] Dal Cason TA. The identification of cathinone and ethcathinone. Microgram 1992,25 (12), 313-317.

[14] Elsohly M.A, Feng S., Salamone S.J, and Wu R. A sensitive GC-MS procedure for the analysis of flunitrazepam and its metabolites in urine. J. Anal. Toxicol.1997,21: 335-340.

[15] hurman EM, Ferrer I, Rodriguez Fernandez-Alba A. Matching unknown empirical formula to chemical structure using LC-ToF-MS accurate mass and database searching: Example of unknown pesticides on tomato skins. Journal Chromatogr A 2005c, 1067: 127-134.

[16] Mou Y, Rabalais J. Detection and identification of explosive particles in fingerprints using attenuated total reflection-Fourier transform infrared spectroscopy. J. Forensic Sci. 2009, 54 (4), 846-850.

[17] Kuptosov A.H. Applications of Fourier Transform Raman Spectroscopy in Forensic Science. J Forensic Sci. 1994, 39, 305-318.

[18] Ferrer I, Thurman EM. Liquid chromatography/time-of-flight/mass spectrometry(LC/ToF/MS) for the analysis of emerging contaminants. Trends Anal Chem 22:750-756.