Drugs of Abuse GC-TOFMS Analysis Applied to Methods Developed for Use in a Local Forensic Crime Laboratory

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1. Introduction

LECO Corporation assisted a local forensic crime laboratory in method development for drugs of abuse analysis utilizing the Pegasus HT GC-TOFMS. There is a crucial need for fast and accurate MS methods to provide definitive identification of suspected drugs in criminal investigations. The laboratory testing presented illustrates highly efficient methods and data developed for crime labs that practically assist in the battle against illegal drugs. Many drug classes have chemical properties that present particular analytical challenges, such as poor detector response, chemical lability, or poor chromatographic peak shape. This article presents GC-TOFMS methods developed with non-derivatized samples for several major drug classes and chemical functionalities. The major drugs included in the initial method development are methamphetamine, ecstasy, and heroin. Robust and accurate analytical methods were developed for clandestine laboratory process samples, identification of confiscated drug substances, and trace level analysis for suspected drug residues.

The benefits of utilizing GC-TOFMS for drug identification analysis include acquiring full range non-skewed mass spectral information, along with fast acquisition rates essential for high throughput analysis. This work demonstrates the ability of GC-TOFMS to increase laboratory productivity and efficiency while providing indisputable positive identifications for illegal drugs analysis in criminal investigations.

2. Experimental Conditions

Initial methods were developed for three major drugs of abuse: ecstasy, heroin, and methamphetamine. Drug samples were prepared by dissolving the suspected material in methanol and retaining the soluble portion for analysis. Analytical results were generated with a LECO Pegasus HT GC-TOFMS. The Pegasus HT GC-TOFMS was equipped with an Agilent 6890 gas chromatograph and Gerstel MPS2 autosampler. LECO ChromaTOF® software with True Signal Deconvolution® was used for all instrument data acquisition and peak identification. An Rxi-5ms 30 m x 0.25 mm i.d. x 0.25 µm film column (Restek Corp, Bellefonte, PA) was used to obtain the necessary chromatographic separation. Helium was used as the carrier gas at a constant flow of 2.0 mL per minute. Various chromatographic temperature programs were developed for specific drug types. The GC temperature program developed for methamphetamine and ecstasy consisted of an initial oven temperature of 100°C for 1.0 minute, followed by a temperature ramp of 15°C per minute, to a final temperature of 280°C held for 2.0 minutes, with a total run time of 15.0 minutes. The methamphetamine/ecstasy samples were introduced into the GC with a 1 µL injection split 200:1 at 250°C. The MS transfer line temperature was maintained at 280°C. The GC temperature program developed for heroin analysis consisted of an initial oven temperature of 120°C for 0.5 minutes, with an initial temperature ramp of 20°C per minute to 200°C, followed by a secondary temperature ramp of 10°C per minute, to a final temperature of 280°C, with a hold time of 5 minutes, for a total run time of 17.5 minutes. The heroin samples were introduced into the GC with a 1 µL injection split 10:1 at 200°C. The MS transfer line temperature was set to 280°C. Uniform mass spectrometer parameters were used for the initial methods. The mass range was set at 45-450amu with an acquisition rate of 5 spectra per second. The ion source chamber was set to 225°C and the detector voltage to 1750V with an electron energy of -70eV.

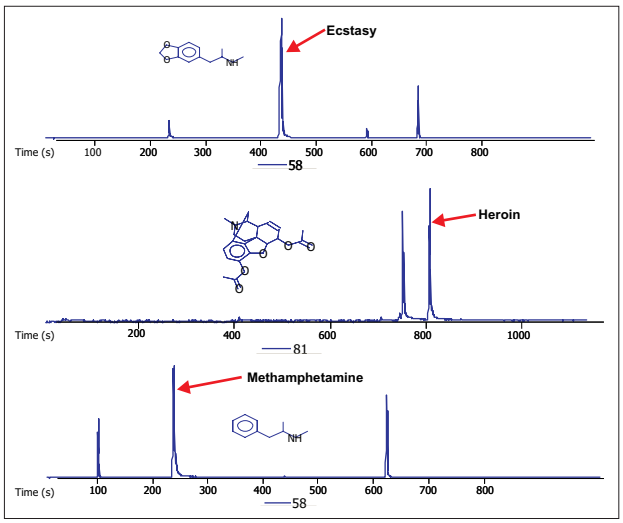

Figure 1. Figure 1 shows the extracted ion chromatograms for Ecstasy (A), Heroin (B), and Methamphetamine (C) by the GC-TOFMS methods developed for routine identification of suspected confiscated drugs.

3. Results and Discussion

GC-TOFMS Analysis

Methods developed for methamphetamine, ecstasy, and heroin were carried out with multiple injections by the Pegasus HT GC-TOFMS system. Analytical results show chromatograms with target analytes labeled according to NIST MS library searches for each drug. Figure 1 (A) shows the extracted ion chromatogram for the drug ecstasy (N-Methyl-3,4-methylenedioxyamphetamine) using the unique mass fragment m/z 58. The peak for ecstasy elutes at 405.6 seconds with a library similarity of 905 out of 999. The extracted ion chromatogram for heroin

(diacetylmorphine) is illustrated in Figure 1 (B) using the unique mass fragment of m/z 81. The peak designated for heroin shows a library similarity match of 887 out of 999. Figure 1 (C) shows the extracted ion chromatogram for methamphetamine using the unique mass fragment of m/z 58. The peak for methamphetamine elutes at 229.9 seconds with a library similarity of 889 out of 999. Both ecstasy and methamphetamine are sympathomimetic amines (basic drugs) which are known to afford poor chromatographic peak shape. Both analytes exhibit quality chromatographic peak performance by the GC-TOFMS analysis. Heroin is known to be chemically labile and prone to loss of an acetyl group forming the compound monoacetylmorphine. Monoacetylmorphine can be observed in the Figure 1 (B) eluting prior to heroin at 701.6 seconds. The method developed shows successful identification of heroin with high library match quality. The methods developed for methamphetamine, ecstasy, and heroin are uncomplicated and robust with analysis run times of less than 20 minutes. They require minimal sample preparation without the need for time consuming sample derivitization.

Experimental "Meth" Process Lab Analysis
Method Development

Law enforcement agencies confiscate multilayer liquid samples from suspected clandestine "meth" labs which are used as extraction solvents in the manufacturing process for methamphetamine. The samples contain an aqueous and volatile layer. Methods were developed to analyze these samples by GC-TOFMS. The GC-TOFMS method used for the "meth" lab process samples was the same column and method parameters as previously developed for the analysis of methamphetamine and ecstasy. The process sample contained two distinct dingy layers. The top volatile layer was filtered and introduced into the GC directly with a 1 µL injection, split 200:1 at 200°C. The aqueous layer was prepared for analysis by extracting a 5 mL aliquot with 2 mL of methylene chloride. The methylene chloride was filtered and introduced into the GC with a 1 µL injection, split 200:1 at 200°C. The mass spectrometer method parameters remained unchanged from the previous methamphetamine/ecstasy analyses.

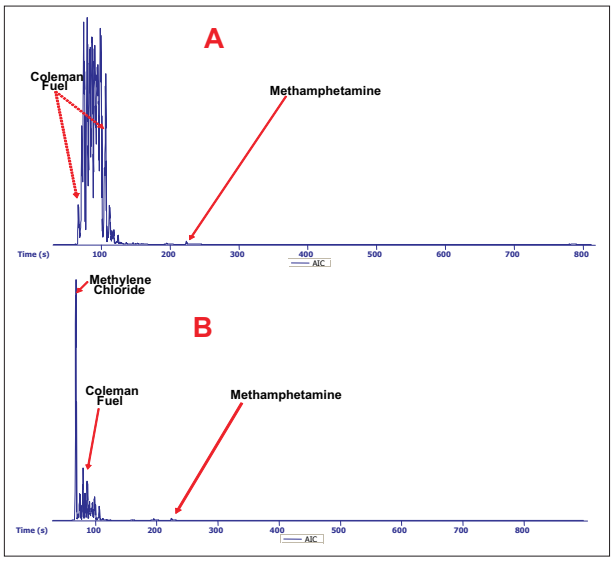

Figure 2. Figure 2 shows the Analytical Ion Chromatogram (AIC) of the methods developed for suspected "meth" process lab samples. The chromatogram labeled (A) is the volatile layer of the "meth" process lab sample. The chromatogram labeled (B) is the analysis of the aqueous layer. Positive identification for methamphetamine is observed in both analyses (A) and (B) at a retention time of 223.7 seconds.

Meth Lab Process Samples Analysis

The results for the "meth" lab process samples show that trace levels of methamphetamine can be detected even in heavy sample matrix. Positive identifications with high library similarity scores were obtained for both the volatile and aqueous layers from the "meth" process lab sample. Methamphetamine was detected with a library similarity score of 817 out of 999 for the aqueous sample and a library similarity score of 916 out of 999 for the volatile sample. Note that the extraction solvent of choice used by many clandestine laboratories is Coleman fuel which is a purified high octane gasoline. The method development and analysis for the "meth" lab process samples demonstrates the ability of GC-TOFMS to provide a straightforward and robust analysis for harsh samples with minimal interference from sample matrices.

Experimental Trace Level Powder Residue Analysis Method Development

Trace levels of powder found in close proximity to suspected drug users are common sample types encountered by forensic crime laboratories. A GC-TOFMS method was developed on a trace amount of powder in a plastic bag found on a drug abuse suspect. The sample was prepared by dissolving the powder in a 200 µL mixture of methanol and methylene chloride. A 50 µL aliquot was transferred to an autosampler vial for analysis. A 2 µL splitless injection was made with the injection port temperature maintained at 250°C. An Rxi-5ms 30 m x 0.25 mm i.d. x 0.25 µm film column (Restek Corp.) was used to obtain the necessary chromatographic separation. Helium was used as the carrier gas at a constant flow of 2.0 mL per minute. The GC temperature program developed for the trace level residue analysis consisted of an initial oven temperature of 100°C for 1.0 minute, followed by a temperature ramp of 12°C per minute, to a final temperature of 280°C, held for 2.0 minutes, with a total run time of 18.0 minutes. The MS transfer line temperature was set to 280°C. The mass spectrometer mass range was set at 45-450 amu with an acquisition rate of 5 spectra per second. The ion source chamber was set to 225°C and the detector voltage was set to 1750V with an electron energy of -70eV.

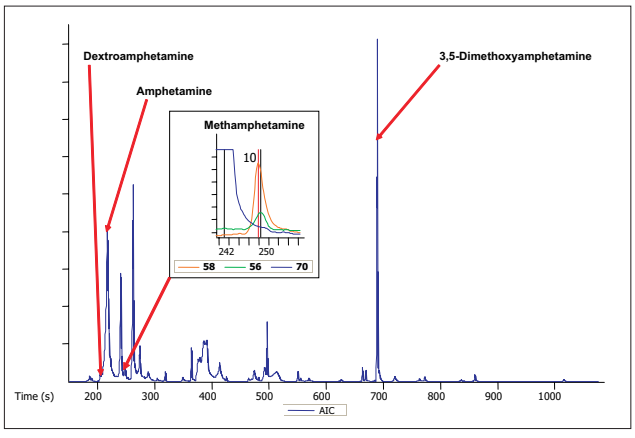

Figure 3. Figure 3 shows the Analytical Ion chromatogram (AIC) for the trace level powder residue analysis by GC-TOFMS. Positive identifications were made for 4 different drugs analytes; dextroamphetamine, amphetamine, methamphetamine, and 3,5-dimethoxyamphetamine as labeled and marked in the chromatogram above. The inset illustrates a trace level peak for methamphetamine that was found utilizing the True Signal Deconvolution® capabilities of the ChromaTOF© software.

Trace Level Powder Residue Analysis

The method developed for trace level residue analysis by GC-TOFMS yielded identification of 40 chemical compounds. Positive identification was made for 4 drugs of abuse; dextroamphetamine, amphetamine, methamphetamine, and 3,5-dimethoxyamphetamine with a high degree of certainty. The results show that GC-TOFMS has the capability to identify trace level residues of illegal substances within contaminating matrices. The inset in figure 3 above shows the unique mass ion chromatogram of m/z = 58 for peak 10 with a positive identification for methamphetamine. This example illustrates the ability of time-of-flight mass spectrometry to acquire non-skewed full range mass spectral data vital for identification of coeluting or partially coeluting low concentration analytes. The method developed for trace level residue analysis demonstrated excellent capability to detect and identify illegal drugs even in heavy sample matrices using GC-TOFMS.

4. Conclusions

This article presents experimental results demonstrating the capability of gas chromatography time-of-flight mass spectrometry to provide simple, robust, efficient, and rapid analytical methods without costly and time consuming sample derivatization for the identification of numerous illegal drugs in a variety of sample types. The results of this work demonstrate that the LECO Pegasus HT GC-TOFMS is a valuable tool that is highly beneficial for crime laboratories in the fight against illegal drugs of abuse. Time-of-flight mass spectrometry provides fast acquisition and high sensitivity while collecting full-mass range spectra enabling accurate library searches of target analytes even in heavy sample matrices as well as areas of serious chromatographic coelution.

Robust and accurate analytical methods were developed for identification of drug products in clandestine laboratory process samples, identification of confiscated drug substances, and trace level analysis for suspected drug residues. This collaborative effort with a local crime laboratory shows the advantages of GC-TOFMS to increase laboratory throughput while providing indisputable definitive identifications for illegal drugs in criminal investigations. These methods are being applied with a LECO Pegasus HT GC-TOFMS at a local forensic crime laboratory as an effective analytical tool in the fight against the rising worldwide drug abuse crime problem.

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