Direct Exposure Probe Analysis on the Pegasus® HT: An Application Compendium

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Key Words: Direct Exposure Probe (DEP), Pegasus HT, Surfactant, Drugs of Abuse, Organometallic, Food and Flavor

1. Introduction

Direct exposure probe (DEP) is a technique for the rapid analysis of a compound which utilizes a filament to vaporize analytes directly in the ionization source as opposed to traditional LC or GC chromatographic techniques. Advantages include the ability to analyze non GC-amenable compounds, such as non-volatile, highly polar, or thermally labile compounds, with minimal sample preparation time and fast sample acquisition times (a few minutes or less). This note is a compendium of various DEP/time-of-flight mass spectrometry applications using direct electron ionization (DEI).

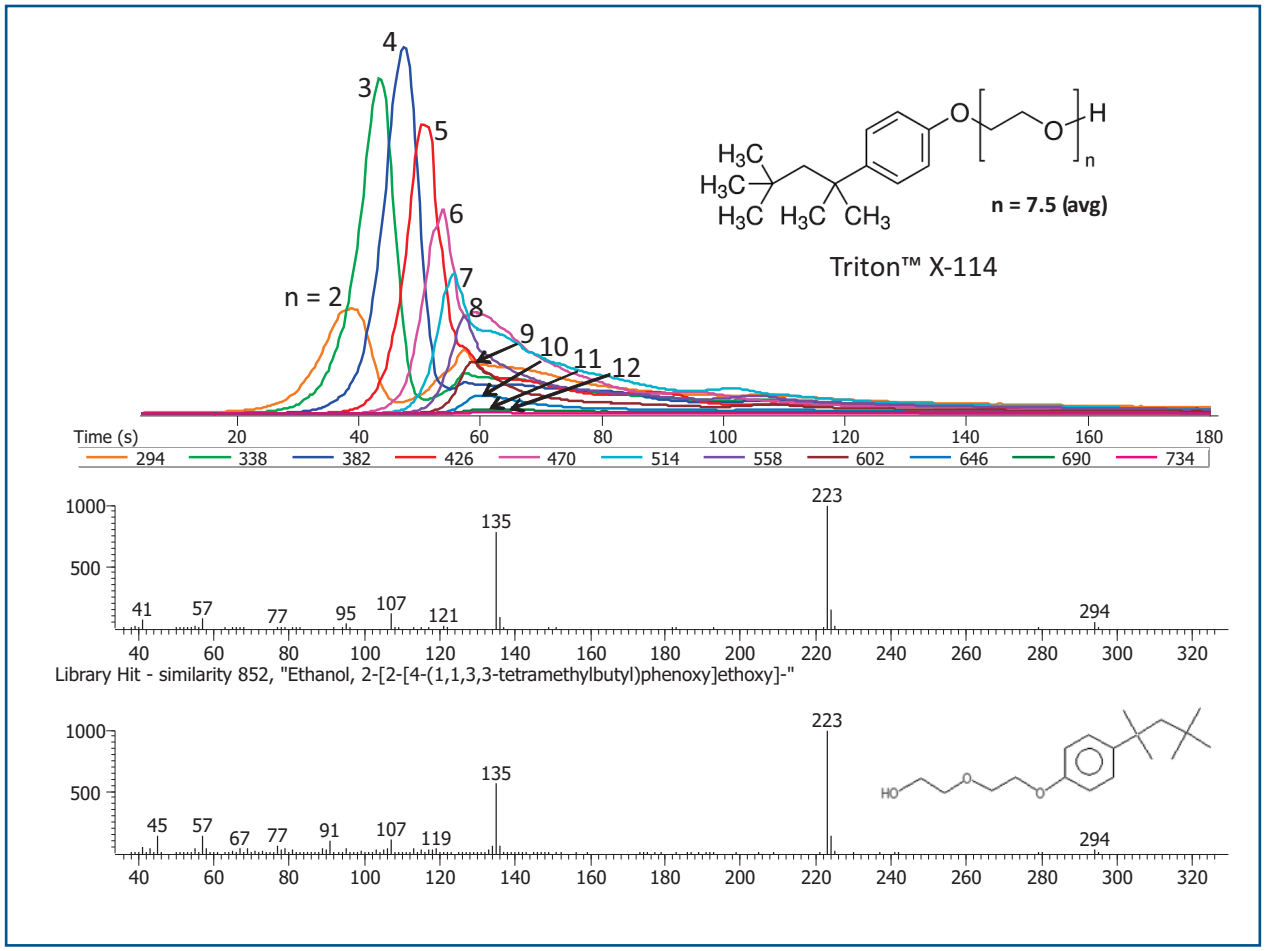

Figure 1. The extracted ion chromatograms (XIC) for the molecular ions of the oligomeric distribution of Triton™ X-114, a non-ionic surfactant, collected by direct exposure probe/time-of-flight mass spectrometry (DEP/TOFMS). The top mass spectrum is of diethylene glycol octylphenol ether by DEP/TOFMS. The bottom spectrum is a corresponding reference spectrum from NIST 14.

Life Science and Chemical Analysis Solutions

Unique benefits of performing DEP experiments on the Pegasus *HT include:*

1. Open ion source design—provides superior robustness and is extremely low maintenance.
2. Time-of-flight mass spectrometry—no mass spectral skewing.
3. True Signal Deconvolution® (TSD®)—identify more unique components even without chromatography.
4. The probe installation does not interfere with the ability to run GC or GC×GC experiments.

The objective of this note was to demonstrate the utility of DEP coupled to LECO's *Pegasus* HT, time-of-flight mass spectrometer (DEP/TOFMS), for a variety of compound classes.

2. Surfactant: Triton X-114 analysis

Triton X-114, polyethylene octyl phenol ether, is a nonionic surfactant with wetting and detergency characteristics that make it suitable for applications like cleaning products, paints and coatings, pulp and paper, textiles, and agrochemicals. A sample of surfactant was introduced to the DEP by touching a wet syringe tip to the DEP filament and allowing to dry prior to analysis. The probe was then inserted into the ion source through the probe vacuum interlock before heating the filament as detailed in Table 1. Full mass range spectra were acquired.

Table 1. DEP-*Pegasus* HT Conditions for Triton X-114 analysis.

Scientific Instrument Services (SIS) Direct Exposure Probe PC-3	
Filament Program	0 A to 1.5 A at 0.5 A/min
Mass Spectrometer	**LECO *Pegasus* HT**
Ion Source Temperature	200°C
Mass Range	35-1000 m/z
Acquisition Rate	3 spectra/s

Triton X-114 is reported to consist of hepta- and octaethylene glycol octyl phenol ether (OPE-7 and OPE-8), with an average molecular weight of 537. The oligomeric distribution of molecular ions from OPE-2 to OPE-12 are shown between 20 and 140 s in the above chromatogram (Figure 1); the mass difference between peaks are consistent with one polymer repeat unit of ethylene glycol (m/z 44). The number average (M_n) molecular weight of Triton X-114 can be calculated from the oligomeric distribution of the molecular ions shown in Figure 1. The M_n measured was m/z 382, corresponding to OPE-4. The discrepancy between the measured and reported molecular weight is most likely because ionization and detection efficiencies decrease with increasing mass, biasing the measured calculation low unless a correction factor is applied.[1] The weight average (M_w) molecular weight can be calculated by leveraging the $[M\text{-}C_5H_{11}]^{\bullet+}$ fragment ions shown in Figure 2, extending the oligomeric distribution to OPE-17. The M_w measured was m/z 536, which correlated well with the reported value (m/z 537). An important note is that this data was collected in 3 mins, highlighting the high-throughput quality of this technique.

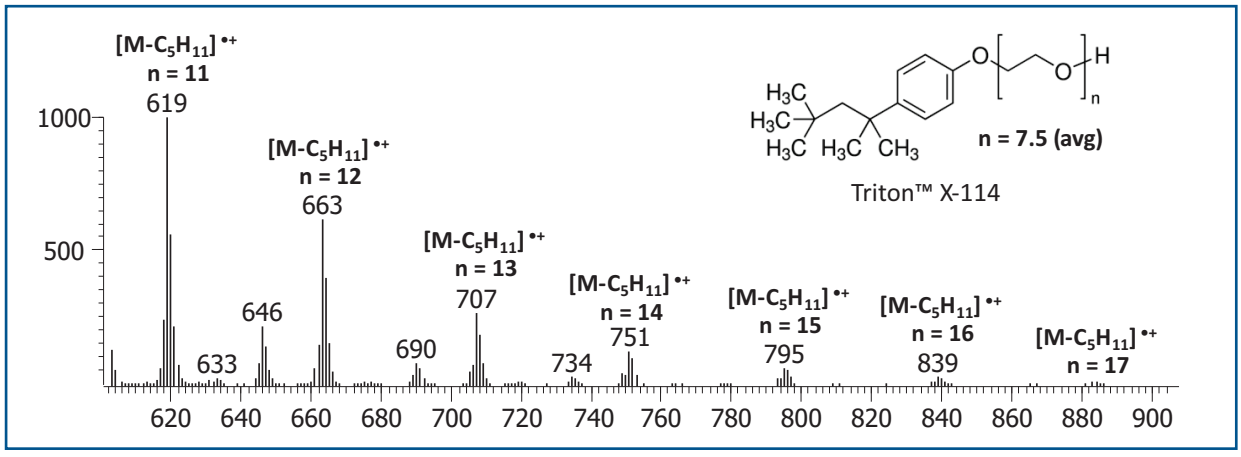

Figure 2. The mass spectrum of Triton X-114 by DEP/TOFMS showing the oligomeric distribution of the [M-C_5H_{11}]$^{\bullet+}$ fragment ions for n = 11 to 17.

3. Organometallic: 1,1'-Bis(diphenylphosphino)ferrocene analysis

The bidentate phosphine ligand 1,1'-Bis(diphenylphosphino)ferrocene (DPPF) is an iron-containing organophosphorous compound, marketed as a "greener alternative" catalyst for a number of cross-coupling reactions. A solution of DPPF was prepared for DEP/TOFMS analysis by dissolving 1 mg of DPPF (Sigma-Aldrich) in 1 mL of chloroform. A small droplet was placed on the DEP filament and allowed to dry prior to analysis. Instrumental details are described in Table 2.

Table 2. DEP-*Pegasus* HT Conditions for 1,1'-Bis(diphenylphosphino)ferrocene.

Scientific Instrument Services (SIS) Direct Exposure Probe PC-3	
Filament Program	0 A to 1.5 A at 1.2 A/min
Mass Spectrometer	**LECO *Pegasus* HT**
Ion Source Temperature	200°C
Mass Range	35-1000 m/z
Acquisition Rate	4 spectra/s

The DEI mass spectrum of DPPF, shown in Figure 3, was collected and searched against the NIST mass spectral database within a few minutes. The similarity score of 872 out of 1000 indicates a very good library match, and validates the applicability of this technique for the rapid analysis of organometallic compounds.

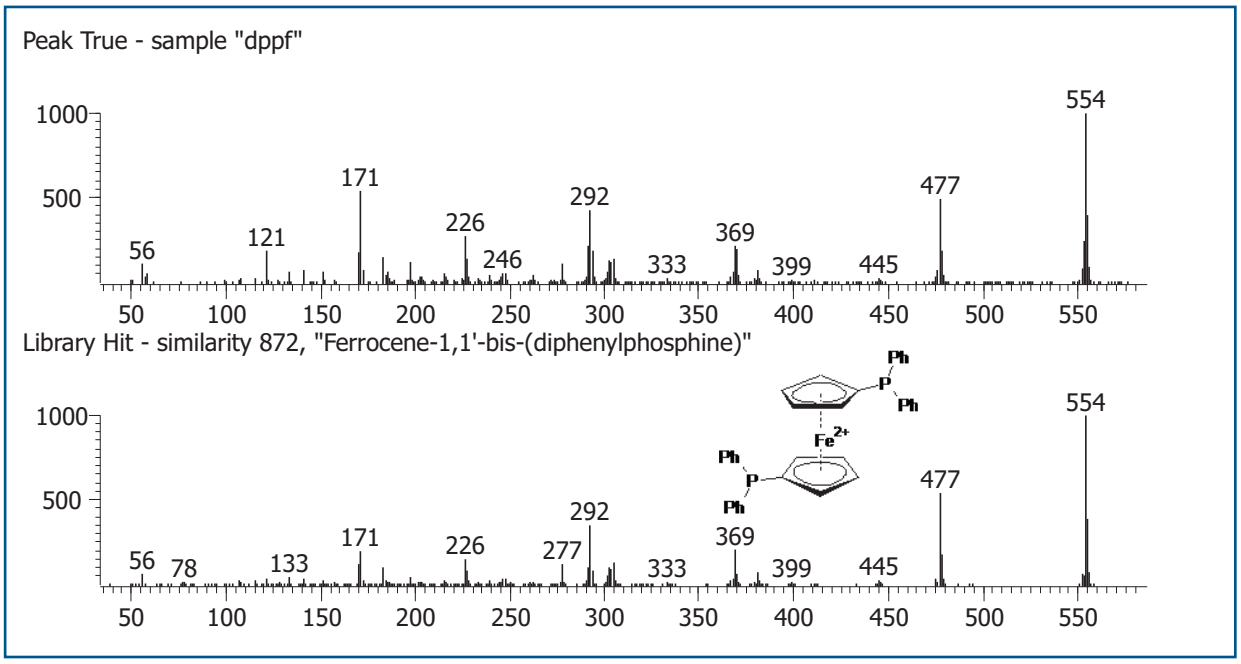

Figure 3. The top mass spectrum of 1,1'-Bis(diphenylphosphino)ferrocene, DPPF , was collected by DEP/TOFMS. The bottom spectrum is a reference spectrum from NIST 14.

4. Forensics: Synthetic Drugs of Abuse

Synthetic cathinones and synthetic cannabinoids are two of the most common classes of synthetic "designer" drugs in the US, often labeled "not for human consumption" to avoid regulation by governing agencies such as the US Food and Drug Administration (FDA). The abuse of these drugs can cause severe health effects, and have resulted in an increasing number of related calls to poison control centers since 2009.[2] The sheer number of these compounds makes their rapid identification critical for treatment as new drugs of abuse rapidly enter the market. A synthetic cathinone, 3-Fluoromethcathinone (ZX-1), and a synthetic cannabinoid, 1-(5-fluoropentyl)-3-(1-naphthoyl)indole (AM-2201), were analyzed by DEP/TOFMS; this technique is extremely useful for confirming the identity of a drug in a timely manner.

About 1 mg of ZX-1 and AM-2201 were each diluted in 1 mL of methanol. Approximately 1 µL of the solution was introduced onto the DEP filament using a syringe. The solvent was allowed to evaporate prior to analysis. Samples were analyzed according to the conditions in Table 3.

Table 3. Pegasus HT Conditions.

Scientific Instrument Services (SIS) Direct Exposure Probe PC-3	
Filament Program	0 A to 1.5A at 1.0 A/min
Mass Spectrometer	**LECO *Pegasus* HT**
Ion Source Temperature	200°C
Mass Range	35-1000 m/z
Acquisition Rate	3 spectra/s

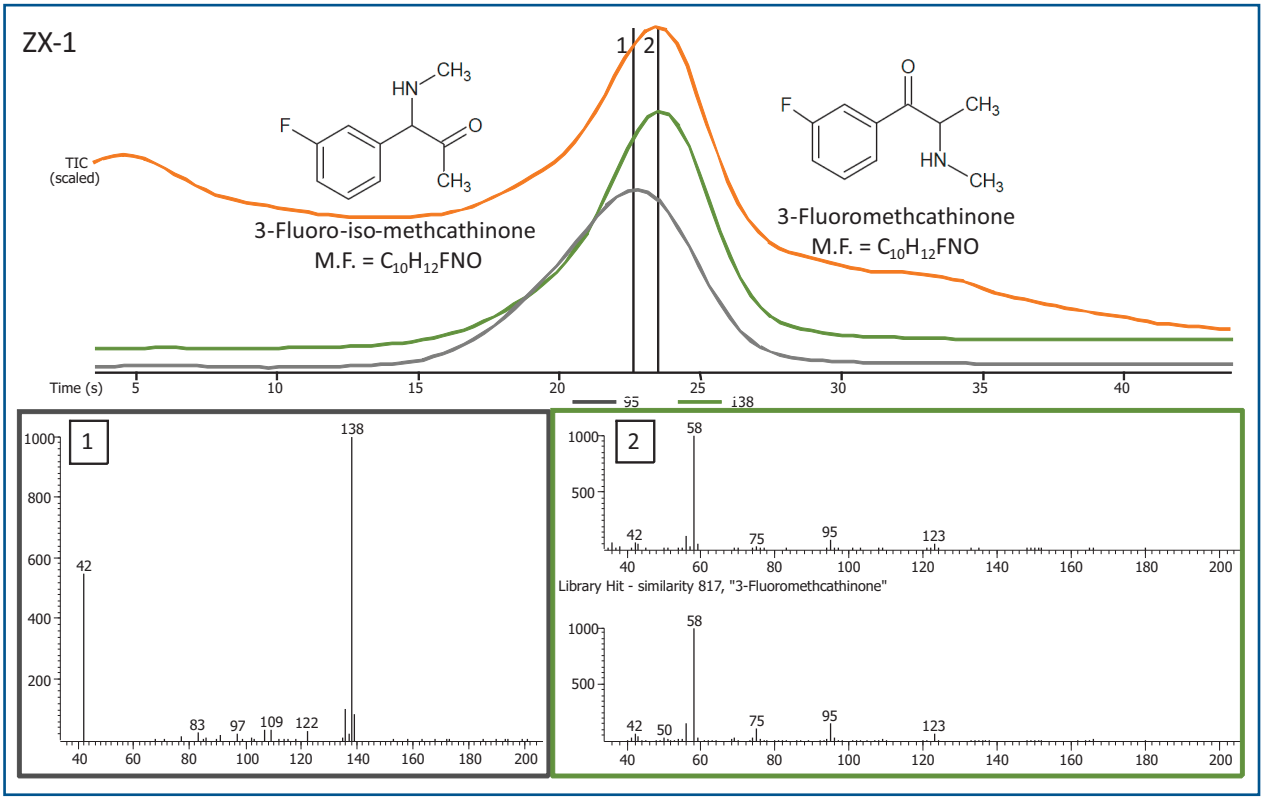

***Figure 4. DEP-TOFMS analysis of ZX-1, a synthetic drug of abuse. The total ion chromatogram (TIC) was intensity scaled graphically to be similar to the intensity of the extracted ion chromatograms (XIC) of two ions distinguishable between 3-Fluoromethcathinone (3-FMC) and 3-Fluoroisomethcathinone (3-FisoMC), identified with* True Signal Deconvolution.**

The active component in ZX-1 is reportedly 3-Fluoromethcathinone (3-FMC), a stimulant drug. The presence of 3-FMC was confirmed within a few minutes by library searching the deconvoluted DEI mass spectra against the NIST, Wiley, and Cayman mass spectral databases; however, an additional component was also detected by deconvolution that was not in the database (Figure 4). A literature search indicated that 3-FMC is enantiomerically impure, often containing 3-Fluoro-iso-methcathinone (3-FisoMC).[3] Peak 1 in Figure 4 matches the mass spectra for 3-FisoMC available in the literature.[3] *True Signal Deconvolution* was able to find the two components in ZX-1, all in less than a minute of analysis time.

The synthetic cannabinoid, AM-2201, was analyzed similarly to ZX-1 as detailed in Table 3. In this case, one clean peak was detected and the mass spectrum was library searched for authentication. The very good similarity score of 859 out of 1000 suggested that the synthetic drug was in fact AM-2201. Notice that the total run time was 3 minutes.

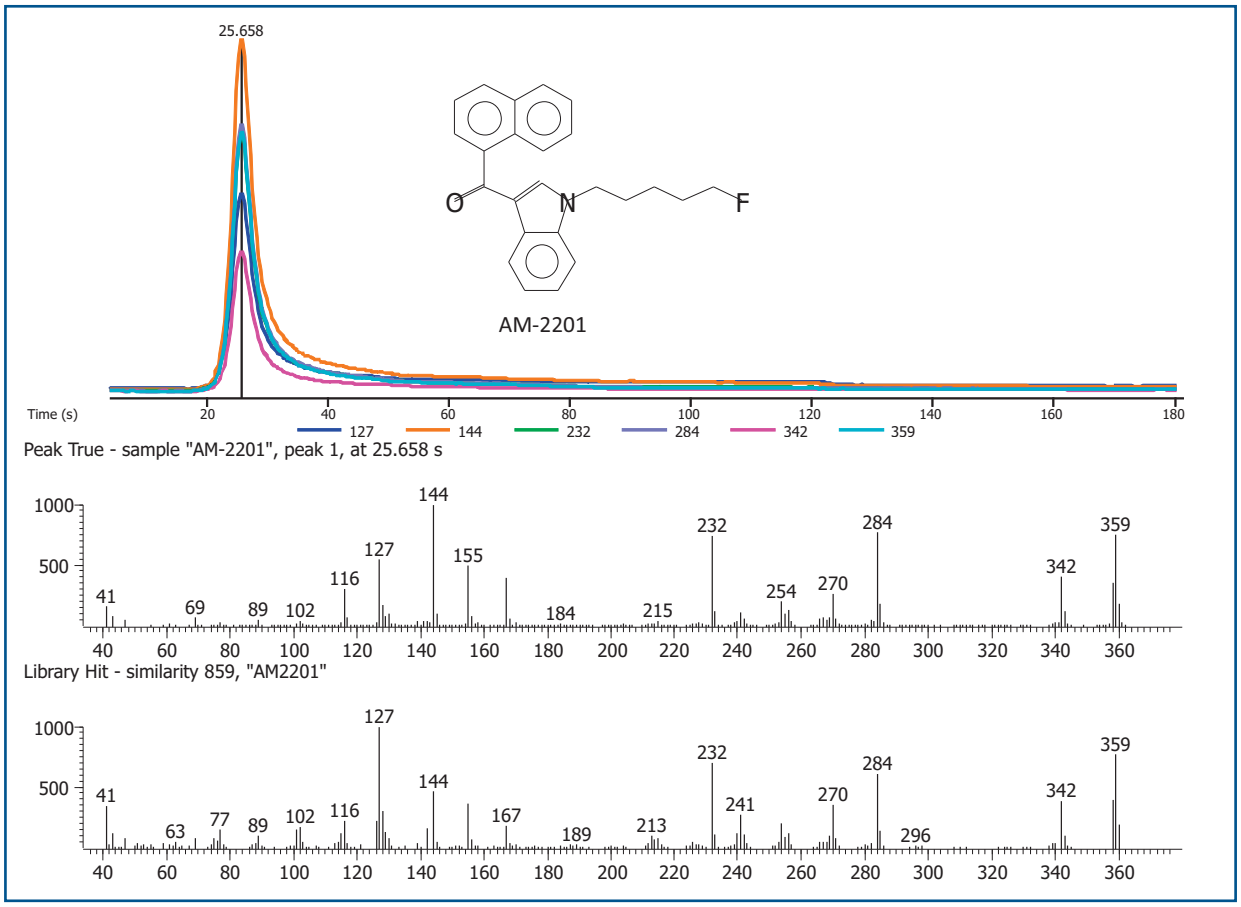

Figure 5. The extracted ion chromatograms of the five most abundant ions in the deconvoluted DEI mass spectrum of AM-2201, with its corresponding mass spectral library hit; the mass spectral similarity was 859 out of 1000.

5. Food and flavor

The analysis of fructose and caffeine was conducted according to the experimental details in Table 3. Approximately 1 μL of a 1 mg/mL solution of each analyte was injected onto the DEP filament using a syringe; the solvent was allowed to evaporate before analysis. The fructose DEI mass spectrum had a very good library similarity score of 864 out of 1000, and the caffeine DEI mass spectrum had an excellent library score of 950 out of 1000. Sugars are difficult to analyze by GC without derivatization, and this example for fructose demonstrates the utility of DEP for the direct analysis of sugars, saving sample preparation and analysis time.

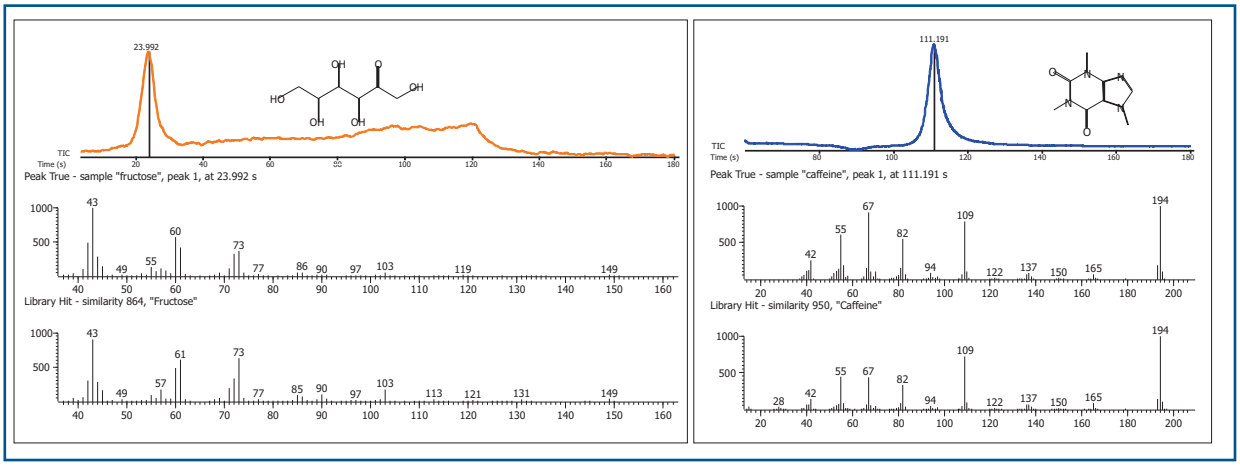

Figure 6. (Left) Total ion chromatogram (TIC) of fructose collected by DEP/TOFMS with its corresponding DEI mass spectrum. The bottom spectrum is the matching reference spectrum from NIST 14. (Right) The DEI mass spectrum of caffeine with its matching library spectrum.

Delivering the Right Results

6. Conclusion

Direct exposure probe coupled to time-of-flight mass spectrometry (DEP/TOFMS) is a very powerful tool for the rapid and reliable analysis of compounds as demonstrated by these examples. An unsurpassed benefit of LECO's system is the ChromaTOF®-GC brand software, which includes *True Signal Deconvolution* that enables the identification of additional components even without chromatographic separation. Furthermore, the open source design of the *Pegasus* HT provides unmatched robustness and is extremely low maintenance compared to any other ion source on the market. These features enable users to extract more information out of their DEP experiments, and in a very timely fashion.

7. References

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[2]*National Drug Threat Assessment. 2011.* U.S. Department of Justice National Drug Intelligence Center. Product No. 2011-Q0317-001. http://www.justice.gov/archive/ndic/pubs44/44849/44849p.pdf

[3]Davies, S., Archer, R. and Ramsey, J. *(2009)* Analytical profiles of methcathinone and related compounds, London Toxicology Group, London. http://www.ltg.uk.net/admin/files/Methcath.pdf

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