# Introduction

#### Background

Direct probe analysis is a common option for the rapid characterization of non-GC amenable liquids or solids having low vapor pressures. The objective of this study was to compare direct probe to Direct Pyroprobe analyses. The benefit of using a Pyroprobe to perform this analysis was the added versatility compared to direct probes. Liquids or solids could be introduced via a quartz tube, or placed directly onto a ribbon filament, and thermally desorbed or pyrolysed. Also, because the Pyroprobe is interfaced directly with the GC inlet, it is possible to perform distillation cut-type experiments or chromatographic separations if required.

## **Direct Exposure Probe/Time-of-Flight MS**

#### Direct Exposure Probe (DEP)

Scientific Instrument Services (SIS) Direct Exposure Probe PC-3. **DEP** Conditions: Filament Program: 0 A to 1.5 A Ramp Rate: 1.0 A/min

#### Mass Spectrometry

Ion Source Temperature: 250°C Mass Range: 35 to 1000 m/z Acquisition Rate: 3 spectra/s

Approximately 1  $\mu$ L of a 1 mg/mL solution of each analyte was injected onto the DEP filament using a syringe, except for Triton™ X-114 which was the neat solution.



Pegasus<sup>®</sup> HT

#### Food and Flavor

The fructose direct electron ionization (DEI) mass spectrum in Figure 1 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.



Figure 1. (Left) Total ion chromatogram (TIC) of fructose collected by DEP/TOFMS with its corresponding direct electron ionization (DEI) mass spectrum. The bottom spectrum is the matching reference spectrum from NIST 14. (Right) The TIC of caffeine and its DEI mass spectrum with matching library spectrum.



# An Alternative to Direct Probe: Pyroprobe<sup>®</sup> Coupled to High Resolution Time-of-Flight Mass Spectrometry

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Figure 2. The extracted ion chromatograms (XIC) for the molecular ions of the oligomeric distribution of Triton X-114, a non-ionic surfactant, collected by DEP/TOFMS. The top mass spectrum is of diethylene glycol octylphenol ether, and the bottom spectrum is a corresponding reference spectrum from NIST 14.



Figure 3. The XICs of the five most abundant ions in the deconvoluted DEI mass spectrum of AM-2201, with its corresponding mass spectral library hit.



Figure 4. 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.

# **Py-HRT (Enhanced Mass Spectral Resolution)**

### Pyrolysis

CDS Analytical Pyroprobe 5200, in the Direct mode, interfaced to a GC-HRT in EI and CI modes. Temperature Program: Interface: 100°C to 300°C @ 100°C/min Pyroprobe: 300°C to 800°C @ 100°C/min Valve Oven and Transfer Line: 300°C

#### Mass Spectrometry

Column: 5 m x 0.18 mm fused silica Oven: 300°C, isothermal Injector: 300°C Carrier: Helium, 20:1 split Mass range: 30 to 1000 m/z Acquisition rate: 3 spectra/s CI: Methane reagent gas (60 to 1000 m/z)

### Food and Flavor

Caffeine yielded similar results for Py-HRT compared to DEP; however, with more confidence due to the sub 1 ppm mass accuracy. Fructose was not successfully measured by Py-HRT.



Figure 5. (Extracted ion chromatogram (XIC) of caffeine collected by Py-HRT with its corresponding Peak True (deconvoluted) mass spectrum. Similarity of 926/1000.

## **Drugs of Abuse**



Figure 6. El and Cl mass spectra of ZX-1, a drug of abuse, collected by Py-HRT. No molecular ion was observed in the EI, which had a library similarity score of 833 out of 1000, but the methane CI data shows an adduct ion corresponding with the correct chemical formula and with excellent mass accuracy (0.16 ppm).







Pyroprobe 5200



Pegasus GC-HRT



Figure 7. Total ion chromatogram (TIC) of a polyurethane foam collected by Py-HRT and its summed mass spectra from 20 to 700 s. The mass spectrum was used to generate a CI-H mass defect plot to help identify halogenated flame retardants added to the foam.



Figure 8. A CI-H mass defect plot of a polyurethane foam collected by Py-HRT. The region in red highlights the halogenated compounds and fragment ions. A few ions from two brominated flame retardants 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) and Bis (2-ethylhexyl) tetrabromophthalate (TBPH) are indicated on the plot by chemical formulas corresponding to the monoisotopic mass of the ion cluster. An organophosphate flame retardant is also shown. The detection of these compounds suggest that the flame retardant added to the foam is likely a Firemaster<sup>®</sup> series flame retardant.

- Direct Pyroprobe is not a substitute for direct probe, but there is some overlap, as well as additional functionality. Direct probes coupled to LECO Pegasus instruments provide unique features:
- Time-of-flight mass spectra which shows little-to-no spectral skewing
- Automatic peak finding and spectral deconvolution for better identification
- Pegasus HT has a very low maintenance source which is beneficial for direct analysis techniques

# Conclusion

