Introduction
There are three main types of high resolution mass analyzers available on commercial gas chromatography instruments, including magnetic sector, time of flight and Orbitrap based systems. All of these instruments are capable of measuring ion masses accurately, but each has its advantages and disadvantages. Typically, researchers consider speed (acquisition rate), sensitivity, and mass accuracy as the key attributes when evaluating the performance of a high resolution mass spectrometer. This presentation reports the collaboration’s work on the high resolution GC/MS system, Agilent 7250 GC/QL-TOF.

Experiments
Materials: Test samples were ordered from either Chem Service (West Chester, PA) or Sigma Aldrich. These included a derivatized carbonyl compounds mixture [M-DCCS414V4], Propiconazole (CAS #: 60207-32-2), Supelco 37 component FAMEs mix (47885-2) and a pesticide standard mixture.

All the samples were analyzed on an Agilent 7250 GC/Qtof-MS system. Data acquisition and analysis software was performed using MassHunter software. All the EI spectra were collected on a dedicated EI only instrument. All the CI spectra were collected on an identical system configured for CI operation in both positive and negative ion modes, using methane as the reagent gas.

Results and Discussion
1. Mass accuracy across dynamic range

The total ion chromatograms collected with EI at both 13 eV and 70 eV show good signal to noise ratios (S/N). The S/N values are higher at the 13 eV compared to the 70 eV, although the absolute ion intensities are lower at 13 eV.

2. Mass accuracy across mass range

Summary of intensities of molecular ions for several compounds at both 13 eV and 70 eV. Generally, the low eV condition was able to produce the molecular ion as the largest or second largest ion in each spectrum. The increase in relative abundance was achieved with an overall decrease in absolute intensities, combined with the observation of fewer low m/z fragment ions, which can prove useful for structure elucidation.

3. Comparison of regular eV and low eV mass spectra of mixtures of aldehydes derivatized with 2,4-dinitrophenylhydrazine (DNPH)

A key upgrade of the new system was the low energy EI source, which is intended to improve ionization efficiency. Low energy EI was used to increase the observation of high m/z ions, for enhancement of molecular ion intensity to assist in compound identification.

4. Methane PCI/MS Analysis of FAMEs (Fatty Acid Methyl Esters)

Supelco 37 component FAMEs mix containing both saturated and unsaturated FAMEs; original concentration was 200-670 μg/mL; diluted 5X for analysis

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5. Methane NCI/MS Analysis of FAMEs (Fatty Acid Methyl Esters)

Mixture of chloro-containing pesticides showed excellent response in negative chemical ionization mode. Mass accuracy was within 3 ppm for all the components at a range of concentrations.

Conclusions
➢ This study evaluated the performance of an Agilent 7250 GC/Qtof-MS in the analysis of unknown impurities present synthetic organic materials using high and low electron ionization, and was well as both positive and negative (methane) chemical ionization.
➢ Overall, the mass accuracy of the instrument was found to be within 2-3 ppm across typical chromatographic peak intensities and mass ranges, which is critical to generating high-confidence molecular formula assignments.
➢ The optimized low energy EI source design increases ionization efficiency. Low energy EI was used to achieve a ‘spectral tilt’ towards high m/z ions to enhance the observation of molecular ions of several compounds. The presence of a molecular ion is still dependent on its stability. It’s suggested to determine molecular mass with alternative approaches (e.g. CI) whenever possible.
➢ It is still of paramount importance to carry out chemical ionization (CI) in order to obtain definitive molecular formula information. Methane PCI and NCI mass spectra proved useful for molecular formula confirmation. It is also a unique tool for selectively detecting a certain type of compounds (e.g. halogenated molecules in complex matrix).
➢ The CI spectra can not only provide exact molecular weight information, but also help structure elucidation of unknowns. For example, the Higher Mw FAMs molecules generate both (M+H)^+ and [M-H]^- ions as shown in the previous experiments.

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