

**A comparison of the structural information contained in  
the LC/MS EI and  
CI spectra of selected chemicals and natural products**

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## Introduction

A series of selected chemicals and natural products were analyzed by both electron impact and positive or negative chemical ionization and the spectra compared for structural content. Natural products analyzed included antibiotics, antioxidants, fats, and glycosides. Chemicals analyzed included selected pesticides, surfactants, and dyes. Compounds were analyzed by both electron impact and chemical ionization. The chemical ionization analyses included both methane and ammonia as reagent gas along with both positive and negative polarities. The spectra generated were examined and compared for molecular weight information, selectivity and sensitivity.

## Instrumentation - Liquid Chromatography and Mass Spectrometry

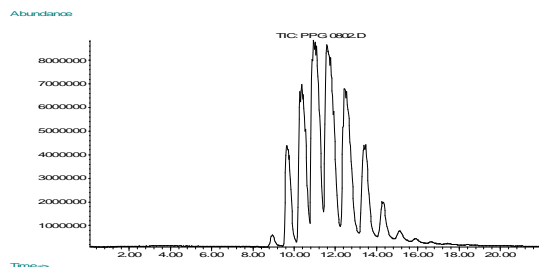
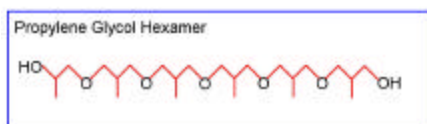
The mass spectrometer used was an unmodified (Agilent Technologies, Inc.) Model 5973 Mass Selective Detector with turbomolecular pump. The HP 5973 is a benchtop quadrupole mass spectrometer with mass range of 1.6 to 800 mass units, 10,000 volt HED, and is available with EI or EICI capabilities, and 6890 GC. The liquid chromatograph used was an HP (now Agilent) Model 1090 LC with manual injector, PV5 pumping system and diode array (pn 79880A) detector. The HPLC column used was a Zorbax SB-C18 (Agilent pn 830990-902), narrow bore 2.1 x 150 mm 3.5 micron. The column was preceded by a Security Guard (Phenomenex, Torrance California) KJ0-4282 guard cartridge kit fitted with one SecurityGuard C184x2.0mm cartridge.

## Instrumentation – Particle Beam Interface

A particle beam interface, Genesis II (CSS Analytical Company, Inc.) was attached to an Agilent 5973 Mass Selective Detector so that samples could be run by LC/MS. Helium is directed into the nebulizer at high pressure coaxially around a capillary containing the LC effluent. At the end of the capillary the helium meets the LC effluent and shears the liquid eluting from the tube into droplets forming an aerosol. The aerosol generated at the nebulizer is sprayed into the desolvation chamber where there is a low vacuum (0.25 to 0.5 atm) and a slightly elevated temperature (50-80 C). The droplets in the aerosol have a high surface area and due to the combination of the vacuum and heat the LC mobile phase is evaporated from the droplets. As the LC mobile phase is evaporated, the sample molecules combine to form a particle. The separation of the LC mobile phase from the sample particles is accomplished through the use of a nozzle with a 2-stage skimmer arrangement forming a momentum separator. Each stage of the separator is attached to a vacuum pump so that the vapor molecules with little momentum will be evacuated as they diffuse away from the center hole of the skimmers. The much larger particles have greater momentum and will not diffuse much while passing through the center hole of the skimmers. The momentum separator is attached to the mass spectrometer ion source through a transport tube. Here the molecules will see a drop in pressure from approximately 0.5 torr to  $4.5 \times 10^{-5}$  torr. Because of this pressure drop gas flow will transport the particles to the mass spectrometer ion source.

## Instrumentation – Data System

The software used for MS control and data analysis was Agilent G1701BA GC/MS Chemstation. The software used for LC control was Agilent G2170AA and G2180AA Multi Technique Chemstation. For LC/MS, the two systems were combined on the same Windows 2000 (Microsoft Corp. Redmond Washington) computer by the Eighty-X Mass Spec Upgrade (CSS Analytical Company, Inc. Shawnee Kansas) software conversion. This conversion by CSS allows the software to “co-reside” and provide concurrent control of both mass spec and liquid chromatograph. The Wiley Registry of Mass Spectral Data 7<sup>th</sup> Edition, with NIST98 Spectra (John Wiley & Son's Inc. New York, New York) was used to search the spectra using pbm matching.



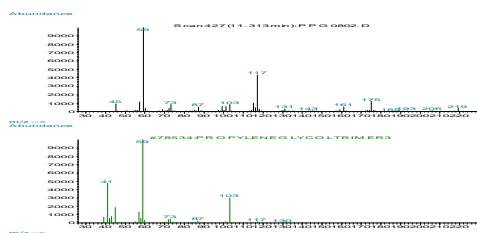


Figure 1a.

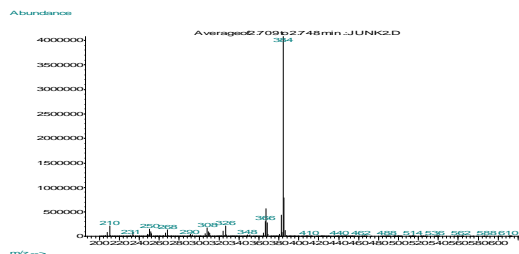


Figure 1b.

Figure 1.

Figure 1a. Propylene glycol hexamer analyzed by electron impact. Library match of the electron impact spectrum of propylene glycol hexamer with the Wiley 7<sup>th</sup> / NIST98 Library. Figure 1b. Propylene glycol hexamer analyzed by NH<sub>3</sub> chemical ionization.

The search of the Wiley 7<sup>th</sup> / NIST98 Library gave mediocre match quality for the electron impact spectrum of propylene glycol hexamer. Note that the molecular ion for propylene glycol hexamer is not observed. For this reason, it was absolutely necessary to analyze propylene glycol hexamer by chemical ionization as this defined the d.p. of the oligomer.

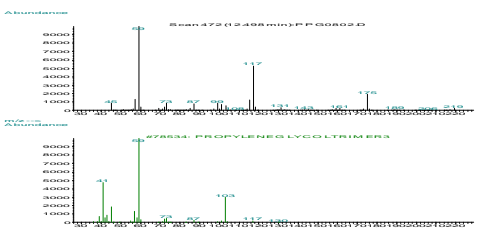
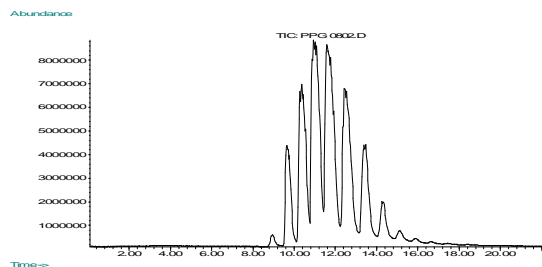


Figure 2a.

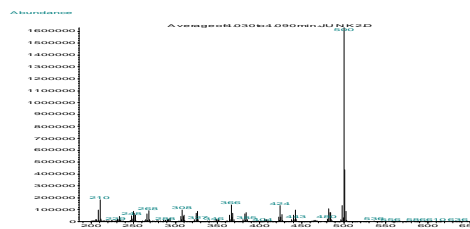


Figure 2b.

Figure 2.

Figure 2a. Propylene glycol octamer analyzed by electron impact. Library match of the electron impact spectrum of propylene glycol octamer with the Wiley 7<sup>th</sup> / NIST98 Library. Figure 2b. Propylene glycol octamer analyzed by NH<sub>3</sub> chemical ionization.

The search of the Wiley 7<sup>th</sup> / NIST98 Library also gave mediocre match quality for the electron impact spectrum of propylene glycol octamer. Note that the molecular ion for propylene glycol octamer is not observed. The electron impact gives the class of compound and the chemical ionization spectrum gives the final identification.

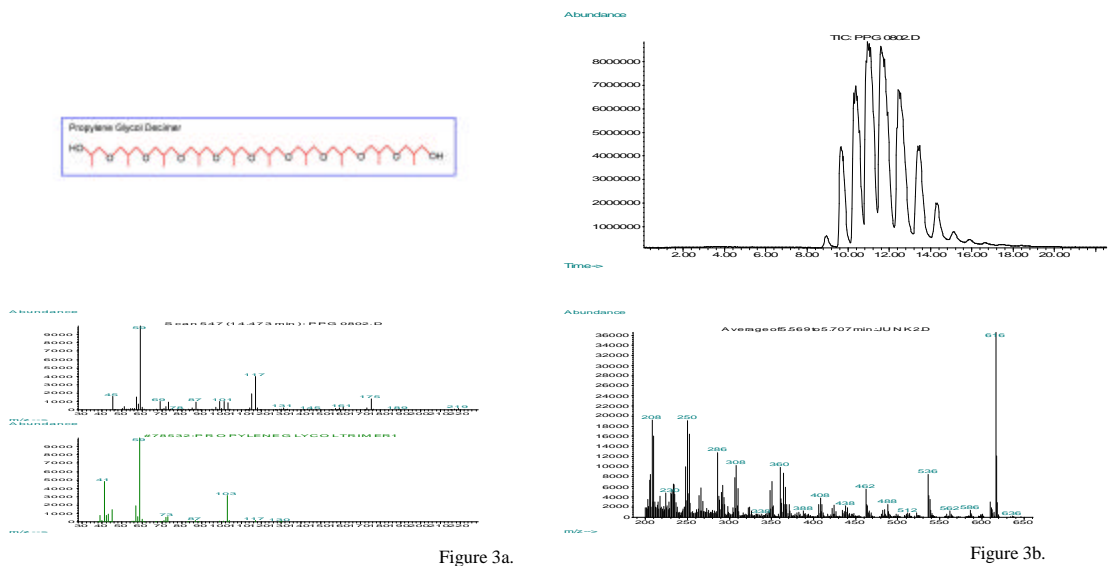


Figure 3a.

Figure 3b.

Figure 3.

Figure 3a. Propylene glycol decimer analyzed by electron impact. Library match of the electron impact spectrum of propylene glycol decimer with the Wiley 7<sup>th</sup> / NIST98 Library. Figure 3b. Propylene glycol decimer analyzed by NH<sub>3</sub> chemical ionization.

The trend continues. Note that the electron impact spectrum gives the class of the molecule and the chemical ionization spectrum gives the final identification that is desired.

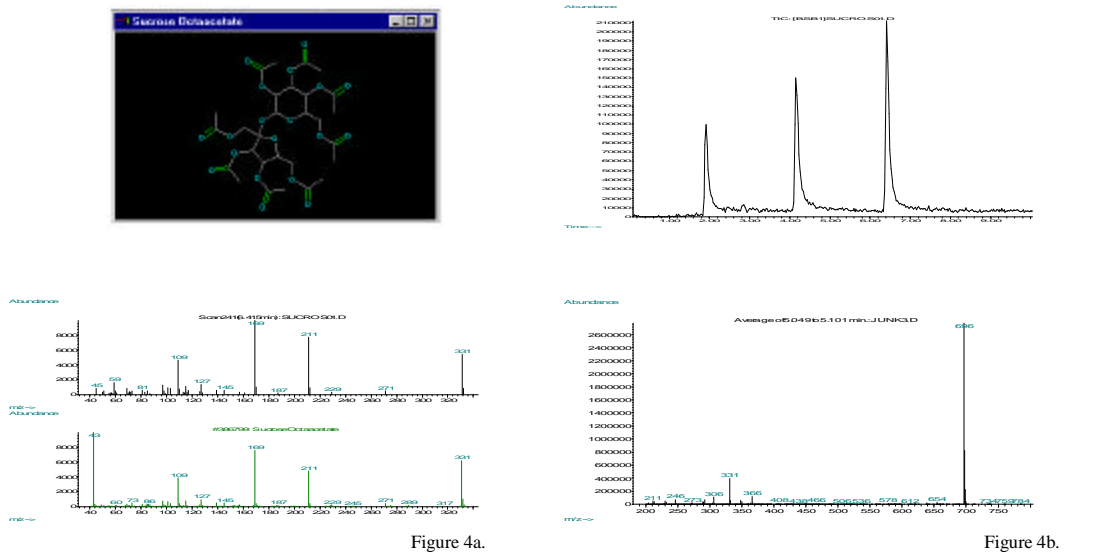


Figure 4a.

Figure 4b.

Figure 4.

Figure 4a. Sucrose octaacetate analyzed by electron impact. Library match of the electron impact spectrum of Sucrose octaacetate with the Wiley 7<sup>th</sup> / NIST98 Library. Figure 4b. Sucrose octaacetate analyzed by NH<sub>3</sub> chemical ionization.

The search of the library gave excellent match quality for the electron impact spectrum of Sucrose octaacetate. Note that the molecular ion for Sucrose octaacetate is not observed. In addition, higher molecular weight acetylated sugars such as raffinose or stachyose give the same 331 ion present in the spectrum of Sucrose octaacetate and the chemical ionization spectrum better defines the d.p. of the sugar.

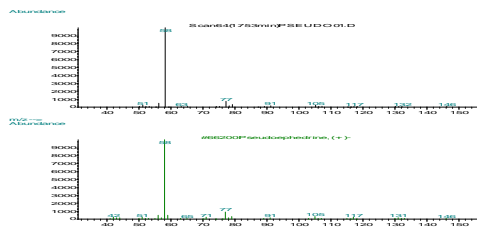
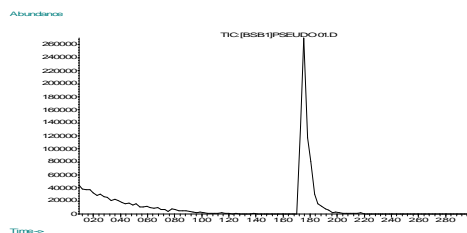
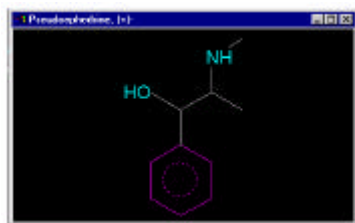


Figure 5a.

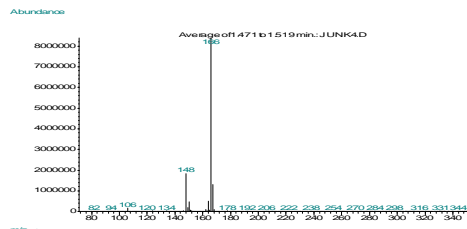


Figure 5b.

Figure 5.

Figure 5a. Pseudoephedrine analyzed by electron impact. Library match of the electron impact spectrum of Pseudoephedrine with the Wiley 7<sup>th</sup> / NIST98 Library. Figure 5b. Pseudoephedrine by NH<sub>3</sub> chemical ionization.

The search of the library gave excellent match quality for the electron impact spectrum of Pseudoephedrine. Note that the base peak of the electron impact spectrum is  $m/z$  58. This  $m/z$  is very indicative of C<sub>3</sub>amines, however it is not selective to Pseudoephedrine. Better selectivity is seen in the chemical ionization spectrum.

## Conclusions

Almost all LC/MS systems today are API electrospray. With this in mind the question is; can the particle beam make a significant contribution to the modern analytical laboratory? The answer is – Yes. The API electrospray lacks a standardized database of cataloged spectra which can be used in the identification of unknowns and can be tricky to use in the analysis of many non-polar molecules. So, for cases where unknown peaks must be identified in a legally defensible manner, nothing matches the ability of electron impact ionization.

Our experiments showed that in some cases even electron impact fails to correctly identify many oligomeric molecules. Our experiments also showed that in order to have all the information to correctly identify an unknown, both electron impact and chemical ionization may be necessary. Evaluation of our experiments showed the following rules.

1. Electron impact is good for identification of small molecules.
2. Chemical ionization is needed for the identification of many fragile and/or oligomeric molecules.
3. Chemical ionization may be preferred for some analysis when the best detection limit is needed for quantitative analyses. This is due to the fact that most of the ion current is accumulated in a single  $m/z$ .

A full reprint of the extended abstract for this poster is available for download at <http://www.cssco.com>