CHEM 5181 Laboratory #2 (prelab) – ESI-quadrupole-TOF Mass Spectrometry

Introduction:

In this lab you will run an electrospray (ESI)-triple quadrupole-time-of-flight (TOF) mass spectrometer from Applied Biosystems, PE SCIEX/ABI API QSTAR Pulsar i Hybrid LC/MS/MS (nickname: Pulsar). In Part I of the experiment, you will analyze an organic compound in both the ESI+ and ESI- modes as well as perform MS/MS (i.e., collision induced dissociation). You also investigate effects some instrument parameters (ESI voltage and nebulizer gas flow rate) have on the signal intensities. In Part II you will analyze a polymer sample and detect and identify multiply charged ions.

You will be provided:

- Simplified instructions for using the Pulsar
- Instructions for the lab
- A methanol solution (~100 ppm) of *trans*-1,2-Diaminocyclohexane-N,N,N',N'-tetra acetic acid monohydrate (abbr. DACTAA)
- A methanol solution (~100 ppm) of polypropylene glycol (PPG), doped with an ammonium salt
- Solutions of formic acid (1% in ACN) and lithium chloride (~mM in ACN)

Description of Instrument Setup:

Refer to the uploaded Lecture Notes of Sept 22 and the course website/"MDS SCIEX/Applied Biosystems API Q-Star Pulsar"/"Instrument Description".

Additional information relevant to the lab:

- ESI capillary: Polymicro Technologies, fused silica capillary tubing TSP075150 (O.D. 154 um, I.D. 74 um), contained in a stainless steel needle, the tip being 9 mm apart from the orifice plane.
- A coaxial flow of nebulizer gas (N_2) is used for the spray needle ("pneumatically assisted ESI").
- A typical mass accuracy for the detection: +/- 0.1 in units of m/z

Summary of Experiment:

I. ESI-MS analysis of DACTAA:

You will examine both ESI+ and ESI- to observe molecular ion signals of DACTAA and study the effect of additives (formic acid and LiCl) on the peak distributions. CID experiments will be performed to obtain information on the structures of the molecular ions as well as of some other species.

With a set value of nebulizer gas flow rate, you will change the spray voltage and determine the onset voltage for electrospray. With a set value of electrospray voltage, you will examine the effect of nebulizer gas flow rate on the signal intensity.

II. ESI-MS analysis of PPG:

You will use ESI+ to ionize the PPG sample and observe distributions of mono- and multiply charged cations. Using the isotope distribution calculator, you compare the observed peaks against theoretical predictions and determine the polymer size.

Prelaboratory Questions:

1. Draw the structure of *trans*-DACTAA. Which of the ESI modes would work, ESI+, ESI-, or both, and why? What is the expected molecular ion(s)?

2. The PPG sample is a mixture of polymers with the formula $(C_3H_6O)_n \bullet C_3H_8O_2$. Draw a general structure. Given the ammonium-rich environment, what ions would you expect to see in the ESI+ mode? Predict monoisotopic peak positions for n = 31 and for mono- and multiply charged (up to 5+) cations.

3. On what parameters does the electrospray onset voltage depend?

4. How does the nebulizer gas work to help improve the ESI signal?

References

P. Kebarle and U.H. Verkerk, *Mass Spectrom. Rev.,* DOI 10.1002/mas.20247 (2009) (course website)
N.B. Cech and C.G. Enke, *ibid*, **20**, 362 (2001) (course website)
D.P.H. Smith, *IEEE Trans. Ind. Appl.,* **IA-22**, 527 (1986)