



# Using electric discharge sources to induce both Atmospheric Pressure Photo-Ionization and Atmospheric Pressure Chemical Ionization.

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## 1.0 Introduction

Atmospheric Pressure Photo Ionization (APPI) describes an ionization technique that utilizes UV irradiation as an energy source to generate ions. Since the first report of potassium photo ions in 1929, photo ionization has evolved into a powerful analytical technique. Today, APPI compliments two common ion sources; Electrospray Ionization (ESI) and Atmospheric Pressure Chemical Ionization (APCI), by extending the range of compounds that can be examined to include some sets of important non-polar molecules. There are two distinct commercially available sources: The PhotoMate<sup>TM</sup> source by Syagen Corporation and the PhotoSpray<sup>TM</sup> source from MDS Sciex. Both sources generate photons from an electrical discharge in low pressure krypton gas. The low pressure krypton gas used in both sources produce photons of 116. and 124. nm (10.6 and 10.0 eV).

In general, PI spectra are noted by their lack of fragments, adducts or other confounding ions. While true photoionization is a one step reaction only producing M<sup>+</sup> as shown in equation 1, many analytes appear as [M+H]<sup>+</sup> indicating Photon Induced Chemical Ionization processes. There are differing views as to the mechanism of the formation of [M+H]<sup>+</sup> ions. The nature of those mechanisms is beyond the scope of this project.

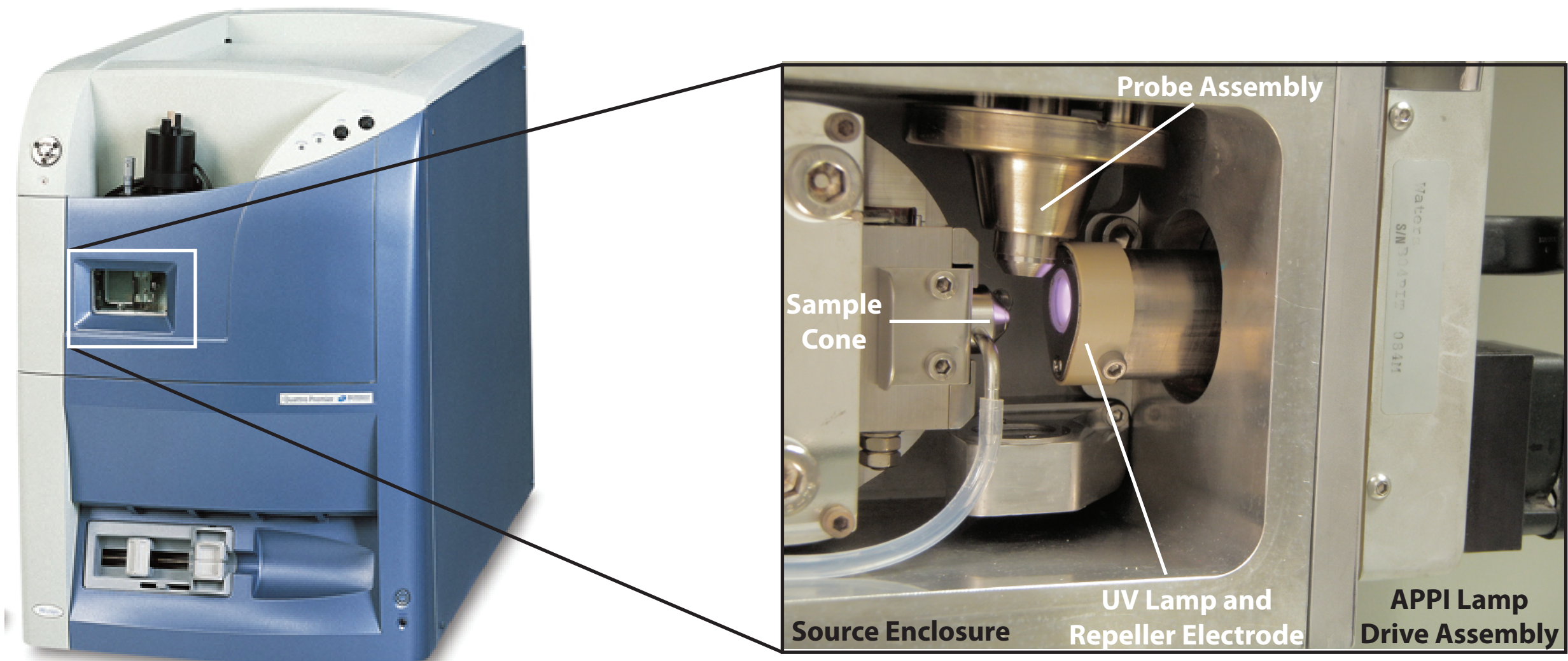


The energy of the photons from krypton discharge lamps is above the ionization potential of most organic analytes but below the potential of most LC solvents. To increase ionization efficiency, a dopant with an ionization potential below the energy of the photon can be added to the solvent to act as a charge carrier between the matrix and the analyte.

Photon emission spectra from pure atomic gases has long been studied. While much of the literature focuses on the strongest emission lines, emission spectra are often continuous over a large range. Work by Lyman and others to characterize photon emission of discharges in various gases found that photons of many wavelengths may be emitted from high pressure discharges. Wavelength selectors have been used with high pressure discharges to restrict the emitted wavelengths to selectively ionize compounds of interest while leaving others. Current low pressure APPI lamps have narrow emission lines.

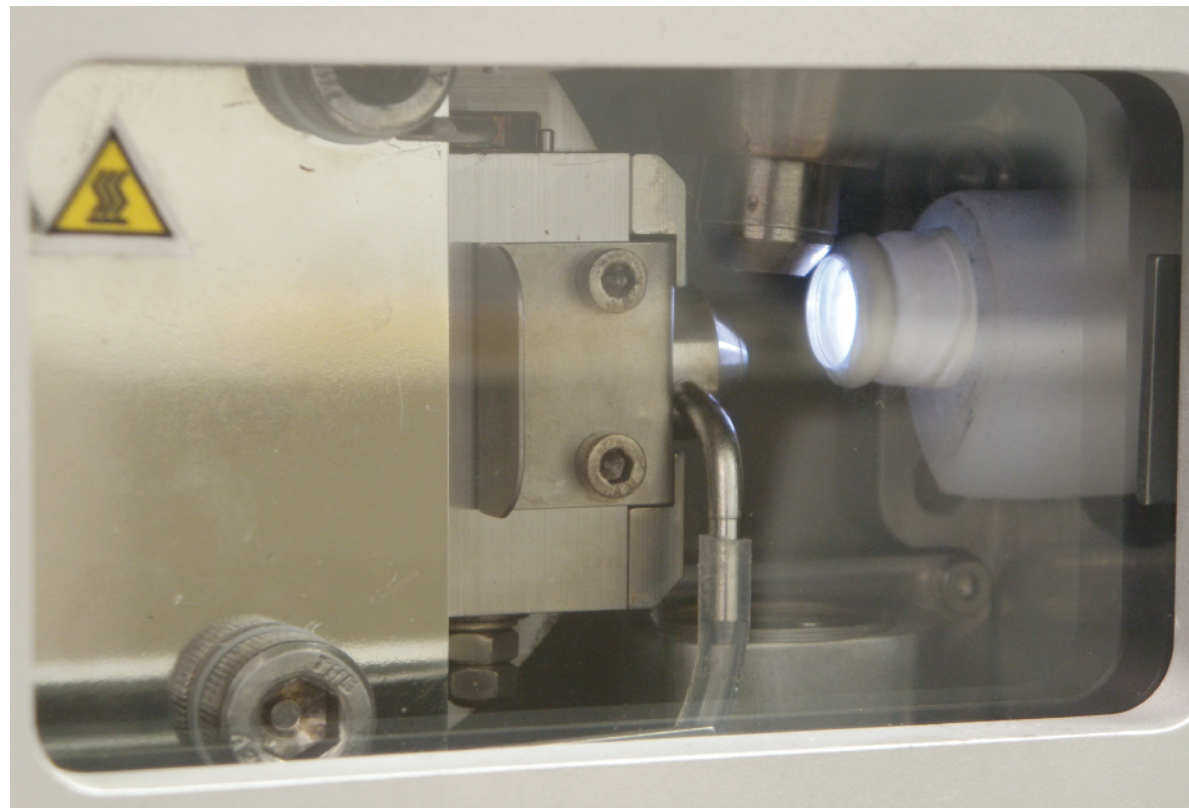
## 2.0 Experimental

Mass spectra were collected on a Waters Quattro Premier LC/MS/MS system shown below. This system is equipped with a PhotoMate<sup>TM</sup> Photoionization source using a krypton discharge.



A series of lightning ion sources were constructed that allowed for testing of different gases, different voltages and currents. One ion source was powered by an Emco DC/DC high voltage converter and another was powered by a Ventex VT12030- 120 neon power supply. A number of electrode types were tested including tungsten and commercial spark plugs. Connections between the power supply and electrodes were made via Champion Spark Plug cables. The discharge tubes were either made of Teflon or a combination quartz/ brass with Tech Steel epoxy putty. A 3 mm thick lithium fluoride window, 10 mm in diameter, could be used or removed at one end of the source. The gases tested were provided by Air Liquide. Gas pressure within the discharge tube was estimated around 1 atm. Spectroscopic measurements were carried out with an Ocean Optics spectrometer. A series of solutions containing pyrene, anthracene, naphthalene and 17a-hydroxyprogesterone were prepared in HPLC methanol and injected manually into a Waters 2695 HPLC system. Instrument parameters, given below, were optimized using m/z 128 of Naphthalene (122 ug/mL). Nitrogen gas was used as the desolvation and cone gas.

APPI Parameters	Commercial Lamp	Lab Built Lamp
Repeller (kV)	1.50	-
Cone Voltage	20	20
Extractor Voltage	7	7
RF Lens	1.0	1.0
Source Temperature (°C)	150	150
Probe Temperature (°C)	250	250
Desolvation Gas (L/hr)	100	100
Cone Gas (L/hr)	30	30



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## 3.0 Results

Figure 1 Photon emission spectra of various gases

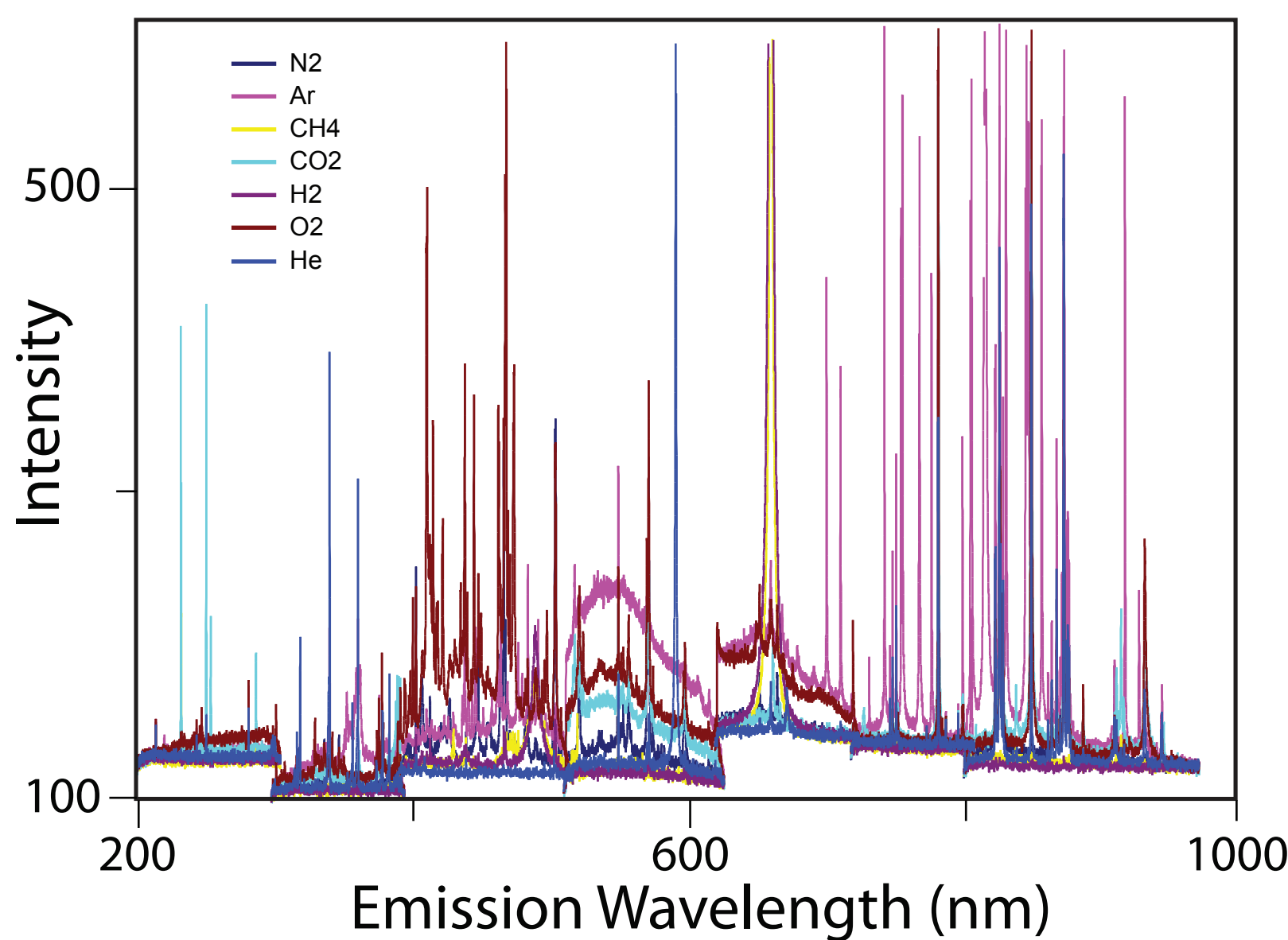


Figure 3 VUV emission of Argon

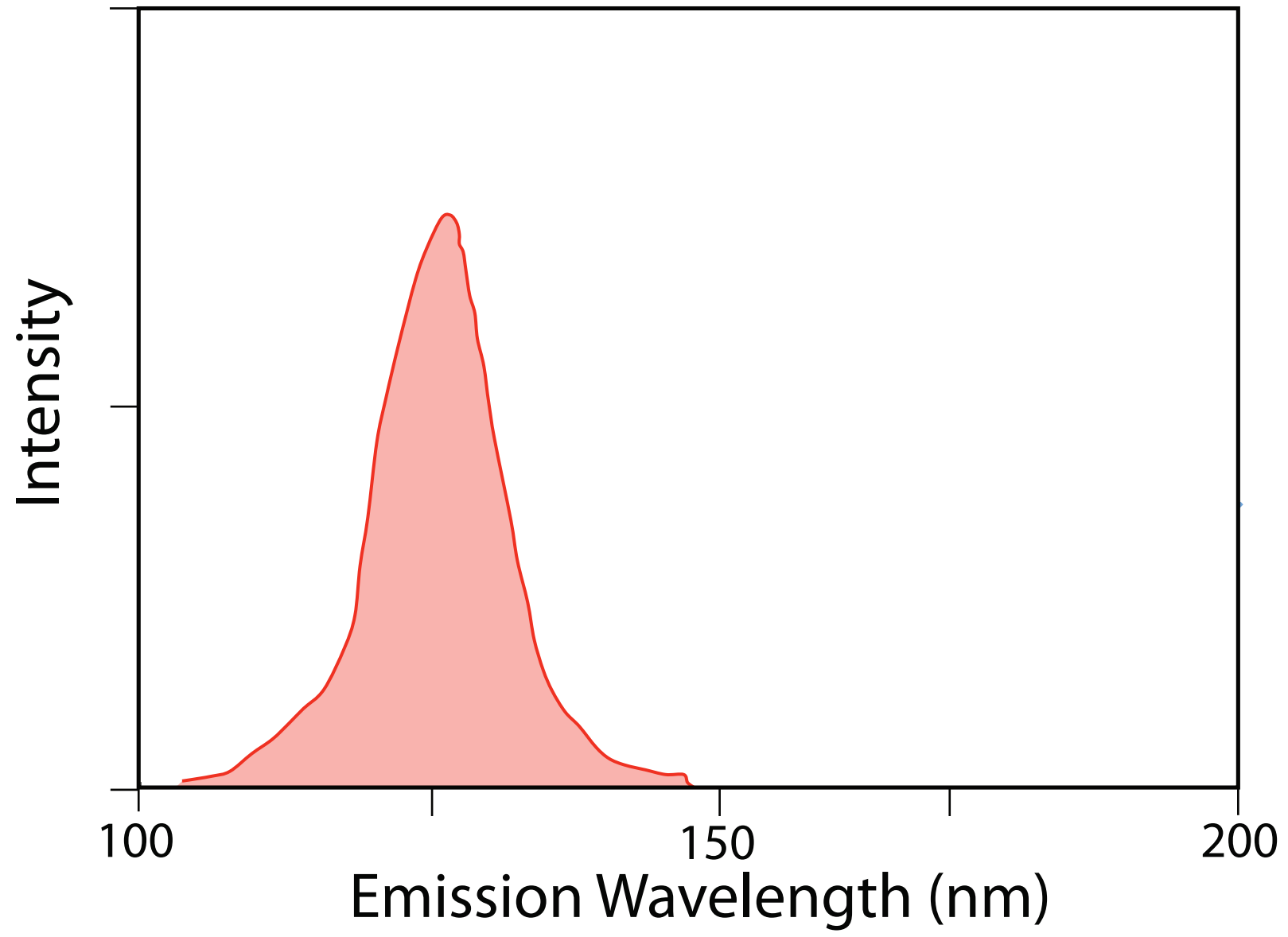


Figure 5 Spectra of Pyrene ionized by Kr lamp

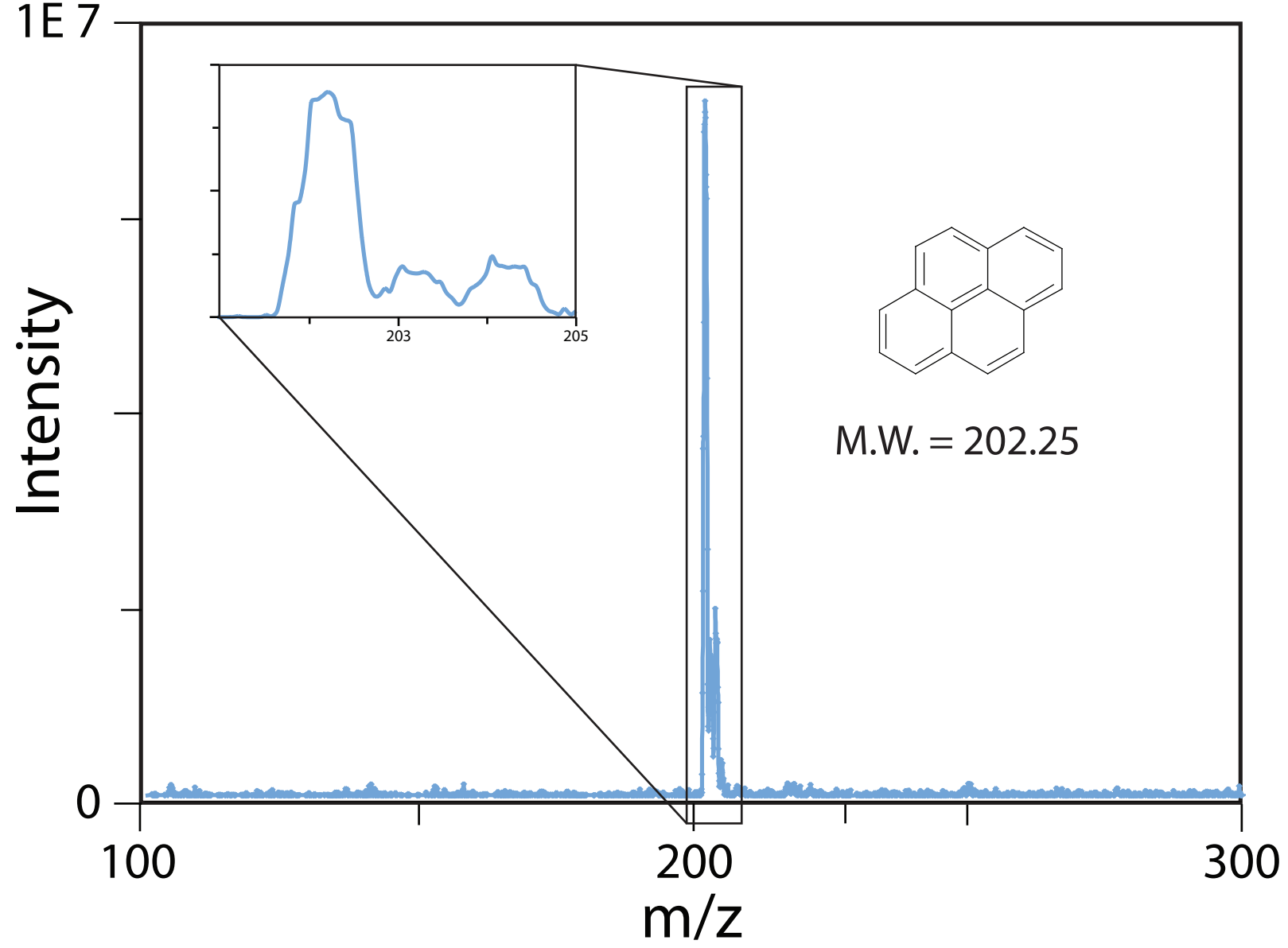


Figure 7 Spectra of 17a-Progesterone ionized by Kr lamp

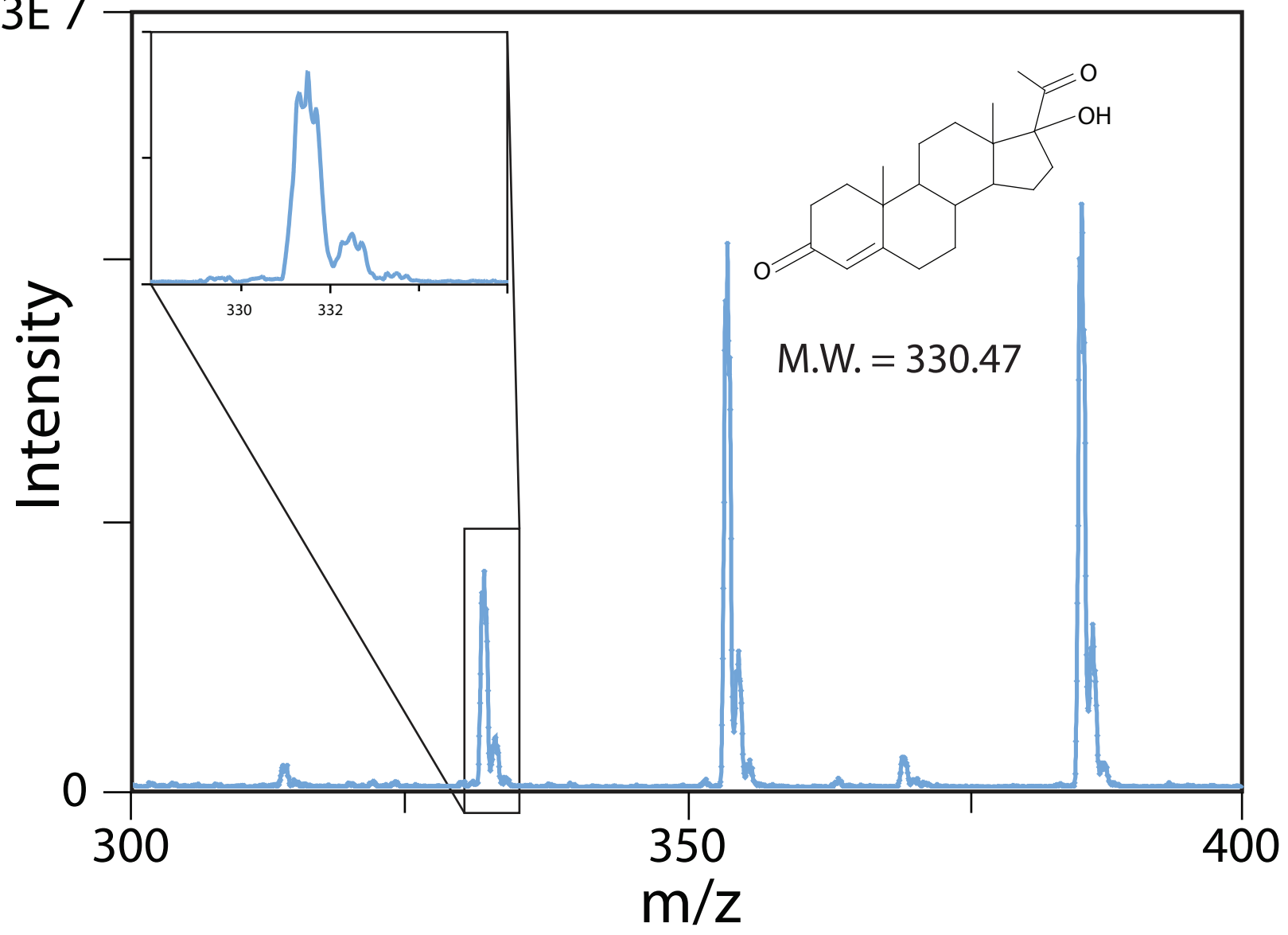


Figure 2 Correlation of N<sub>2</sub> emission lines with reference lines

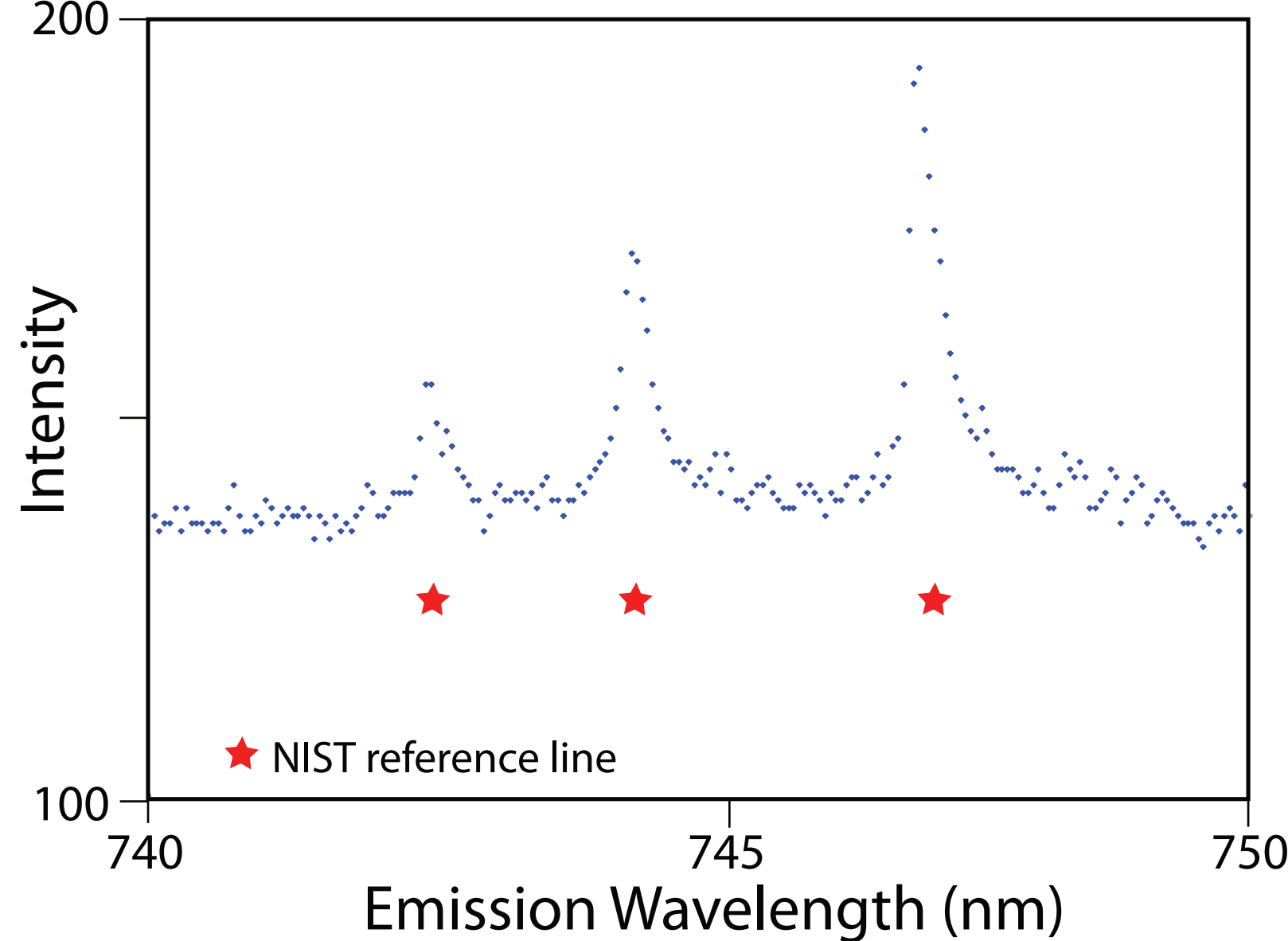


Figure 4 Calibration curves of various gases and Kr lamp

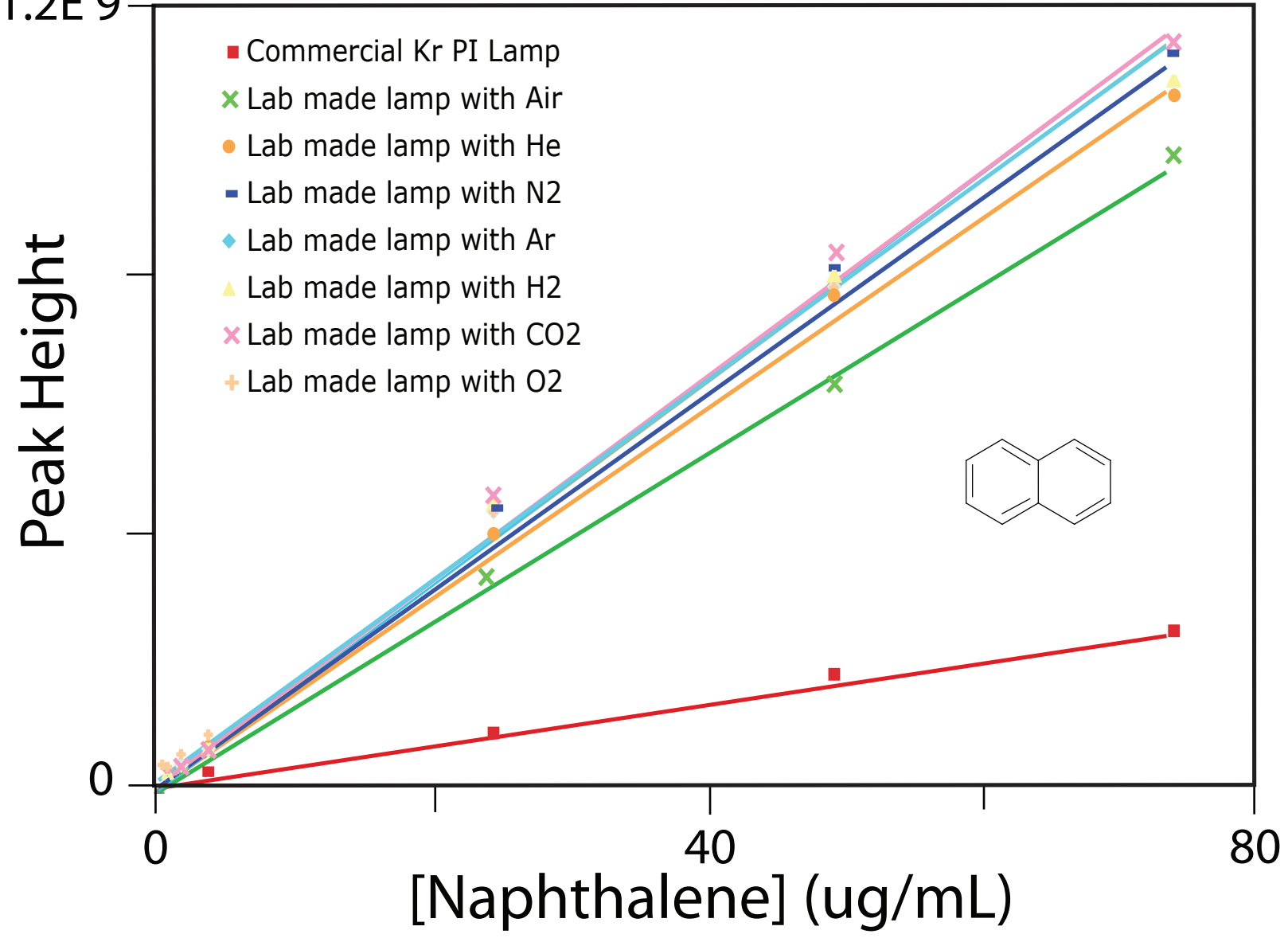


Figure 6 Spectra of Pyrene ionized by lab built lamp

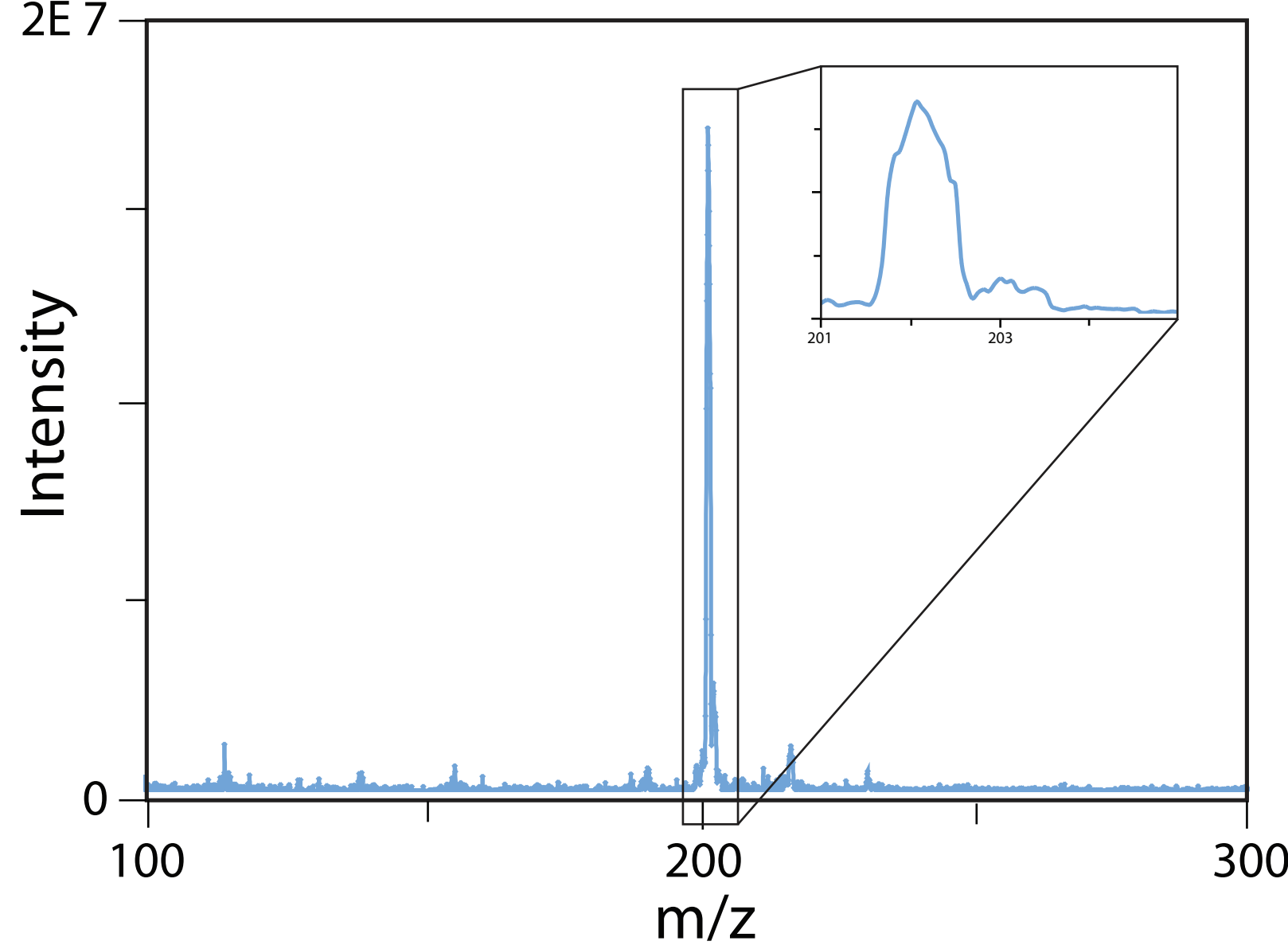
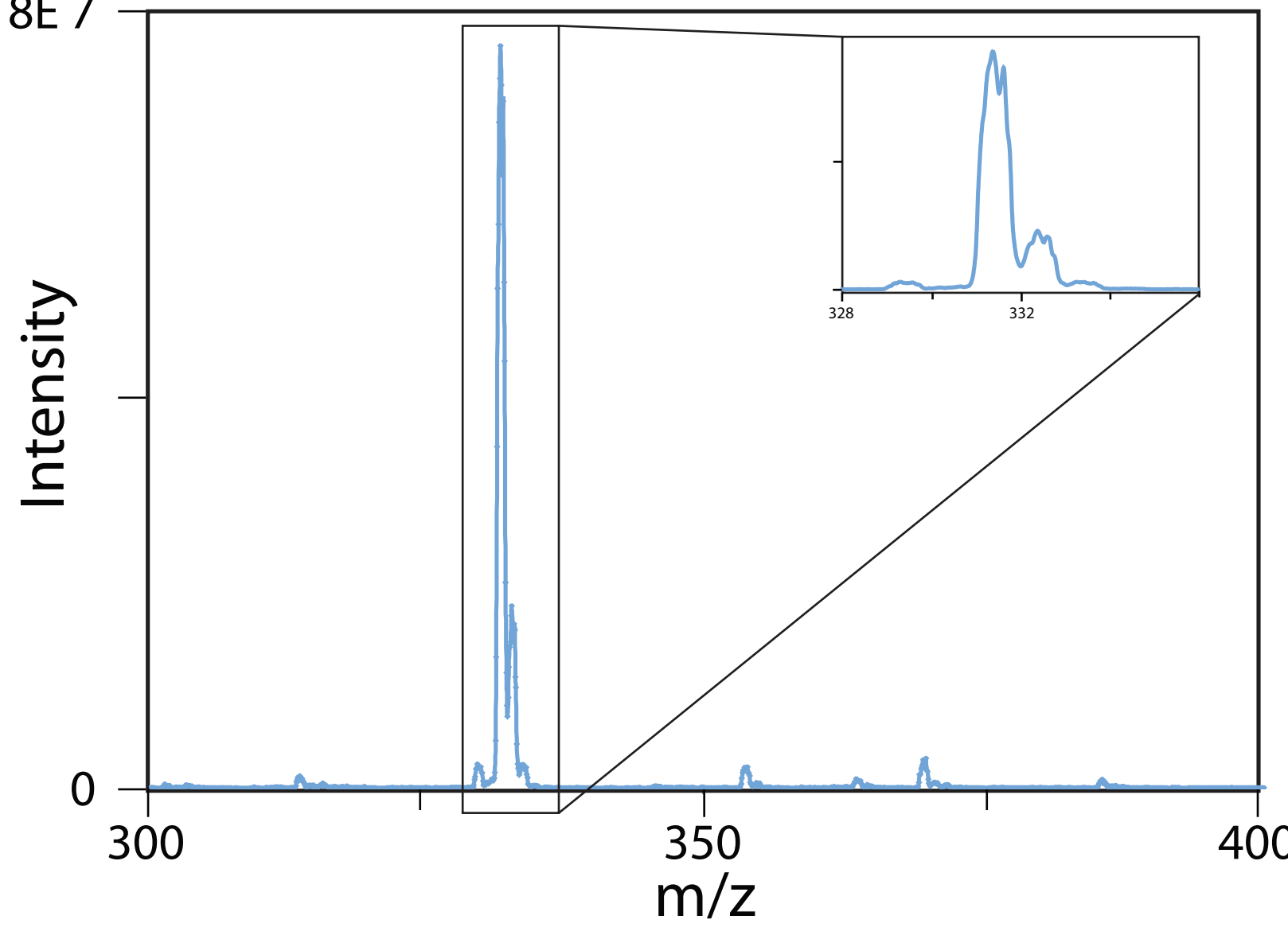


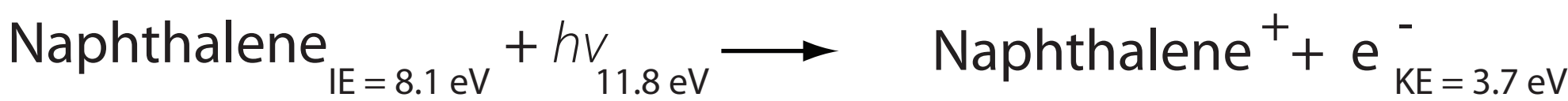
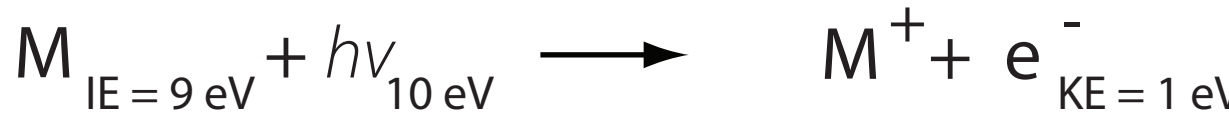
Figure 8 Spectra of 17a-Progesterone ionized by lab built lamp



## 4.0 Discussion

We believe that these results indicate that many electrical discharge based sources produce appropriate photons to induce ionization. The analyte mass spectra was found to be similar between our lab built lamps and the commercial krypton photoionization lamp indicating the mechanism and nature of the photon induced chemistry is similar between the two. The similarity of the mass spectra produced by different gases supports our belief that ionization can be independent of gas type.

From the photoelectron effect, the source of the photon doesn't matter, as long as the energy of the photon is greater than the ionization potential of the analyte. Any energy, from the photon, that is in excess of the ionization potential of the analyte, leaves as kinetic energy in the departing electron. Accordingly, when a krypton lamp is used; the following two equations can be written:



Emission spectra from each of the six gases tested were found to have numerous emission lines in the UV and visible regions. Many of the emission lines agreed with reference spectra. Argon was found to have a large broad emission profile in the vacuum UV region. Even though it was not measured, we believe that all of the gases tested, in our high pressure set up, would have significant VUV emission profiles from 100 to 200 nm.

The ionization ability of emitted photons of the gases tested was found not to vary from discharge gas to discharge gas. We suspect that the nature of the high pressure discharges produce a much larger continuum of emission than low pressure discharges. In fact, all of the gases showed slightly increased sensitivity over the commercial photo ionization lamp tested. We believe that the photon flux is a function of the current of the discharge and that the power supplies used allowed for greater generation of photons than the commercial unit tested.

When a lithium fluoride window is used only photons with wavelengths above 105 nm (11.8 eV) can pass through the window and contribute to ionization but when the lens is removed, photons below 105 nm and any ions or metastables can also contribute to ionization.

## 5.0 Conclusions

A simple and inexpensive PI source was constructed and tested. The similar sensitivity and mass spectra between the lab built and commercial sources support our belief that simple and inexpensive photon sources can use any number of discharge gases.

## 6.0 Acknowledgements

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## 7.0 References

- Robb, D., Covey T., Bruins A., Atmospheric Pressure Photoionization: An ionization method for liquid chromatography-mass spectrometry, Anal. Chem., 2000; 72: 3653.
- Hanold K. et al., Atmospheric Pressure Photoionization. 1 General Properties for LC/MS, Anal. Chem., 2004, 76, 2842-2851.
- Raffaelli, A., Saba, A., Atmospheric Pressure Photoionization Mass Spectrometry, Mass Spectrometry Reviews, 2003, 22, 318-331.
- Ditchburn, R., et al., Ionisation of Potassium Vapour, 1929, Proc Royal Soc, 27, 516-536.
- O'Brien, R. et al., Role of Non-ionizing Photon Absorption in the Observed Mass Spectra produced by an Atmospheric Pressure Photoionization - LCMS Source, ASMS 2007.
- Poschenrieder, W., Warneck, P., Mass Spectrometric Gas Analysis Utilizing Selective Photoionization, Anal. Chem., 1968, 40, 383-390.
- Webb, J., Analytical Photoionization Mass Spectrometer with an Argon Gas Filter between the Light Source and Monochromator, US Patent 3,521,054, 1970.
- Lyman, T., The Spectrum of Helium in the Extreme Ultra-violet, Astrophysical Journal, 1924, LX, 1-15.
- Millikan, R., Bowen, S., Extreme Ultra Violet Spectra, Phys Rev., 1924, 23, 1-38.
- Kersten, H., et al., VUV Photoionization within Transfer Capillaries of Atmospheric Pressure Ionization Sources, ASMS 2010.
- Ralchenko, Yu., Kramida, A.E., Reader, J., and NIST ASD Team (2008). NIST Atomic Spectra Database (version 3.1.5), [Online].

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