

1 Introduction

*Nutraceuticals are a rapidly growing industry dedicated to providing alternatives to traditional pharmaceuticals and healthcare practices. Defined as vitamins, minerals, herbal products or specially treated foods, nutraceuticals claim to improve health and are readily available in a wide variety of dosages and forms.

*Despite their popularity, the term nutraceutical is not recognized by the FDA, and therefore they are considered dietary supplements without any unique regulations or standards.

*Direct Sample Analysis (DSA), a new commercially available ambient ionization source, coupled with a Time of Flight (TOF) mass spectrometer offers a quick and effective analysis of nutraceutical products.

*Methods were developed for the analysis of standards for five common nutraceutical products; Melatonin, L-Carnitine, Co-Enzyme Q, Riboflavin and Ascorbic Acid and can be applied to commercially available products.



Figure 1: Assorted nutraceutical capsules

2 Significance

There is no guarantee of the purity of nutraceutical products due to the lack of FDA regulation. Without adequate information about what specifically is being ingested, people run the risk of some severe medical reactions. Melatonin is a hormone found in plants and animals that regulates circadian rhythms and is a powerful antioxidant. It is taken as a sleep aid, but may affect blood pressure, blood sugar, clotting and cause drowsiness and sedation. Allergies to melatonin are also linked to skin reactions and autoimmune hepatitis. It would therefore be imperative for someone with a pre-existing medical condition interested in taking melatonin to know the exact dosage and ingredients that would be entering their body.



3 Direct Sample Analysis

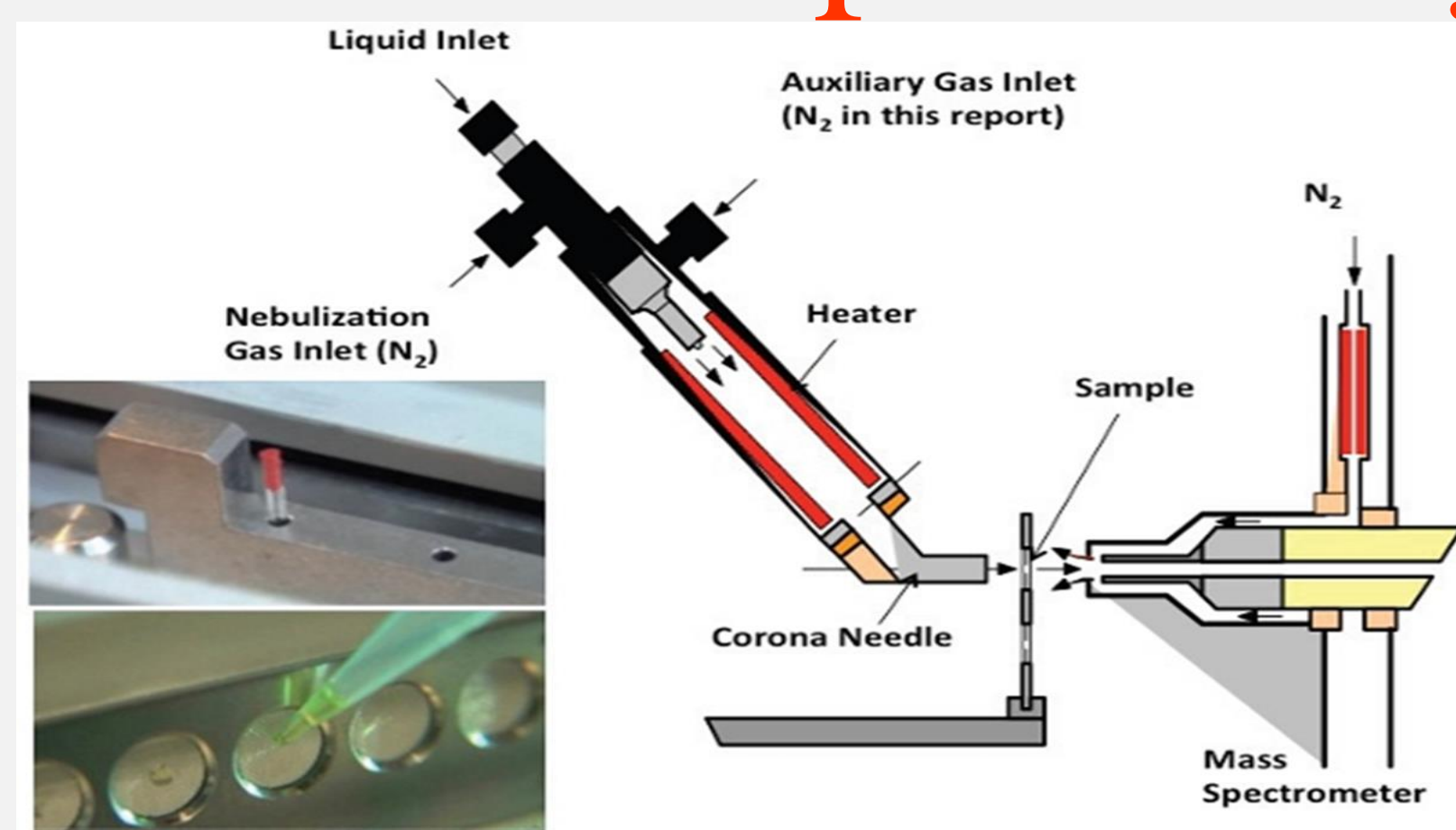


Figure 2: DSA setup schematic, pictures of sample screens and capsules³

A PerkinElmer AxION DSA system was used to introduce the nutraceutical samples into the mass spectrometer. DSA is a form of ambient ionization that functions with a mechanism similar to Atmospheric Pressure Chemical Ionization (APCI). The system requires little to no sample preparation or length chromatography procedures prior to ionization and maintains integrity of the sample. DSA utilizes a nitrogen gas flow and a corona needle to create ions that can then be separated based on their mass to charge ratio.

4 TOF Mass Spectrometry

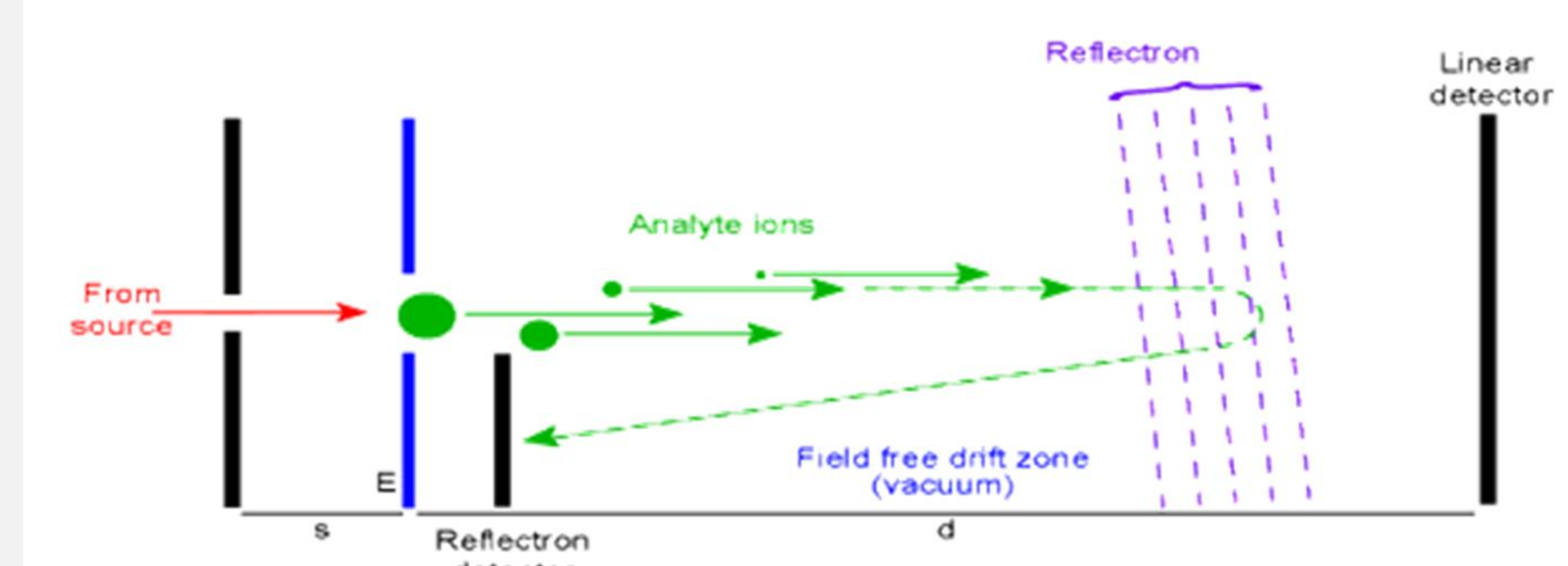


Figure 3: Time of Flight ion path schematic⁴

Time of flight (TOF) mass spectrometry determines an ion's mass to charge ratio based on a measurement of the time it takes to travel through an applied electric field of a known strength. The kinetic energy of the ion will be the same for all ions of the same mass to charge ratio and therefore by determining the velocity of the ion as it travels through the mass spectrometer, its mass can be extrapolated.

5 Instrument Parameters

Instrument conditions are selected and optimized using a software control system. The NexION program allows for specification of the method and selection of m/z ratios of interest.

Parameter	DSA-TOF Setting
Low m/z	100
High m/z	1000
Ion Polarity	Positive
Ion Source Type	DSA
Cylinder Lens	400 V
APCI Voltage	-2500V
APCI Vaporizer Temperature	300°C
Drying Gas Flow Rate	0
Nebulizer Gas Pressure	80 Psi

6 Method

A one mg/mL in water solution was made for each of the dry nutraceutical standards. Twenty microliter droplets were placed on the DSA screen and allowed to dry for fifteen minutes prior to analysis. A capillary exit voltage ramp was performed on each of the standards, and the spectra were analyzed to determine which voltage produced the strongest peak intensities for the desired m/z ratio and lowest additional noise.

7 Standard Spectra

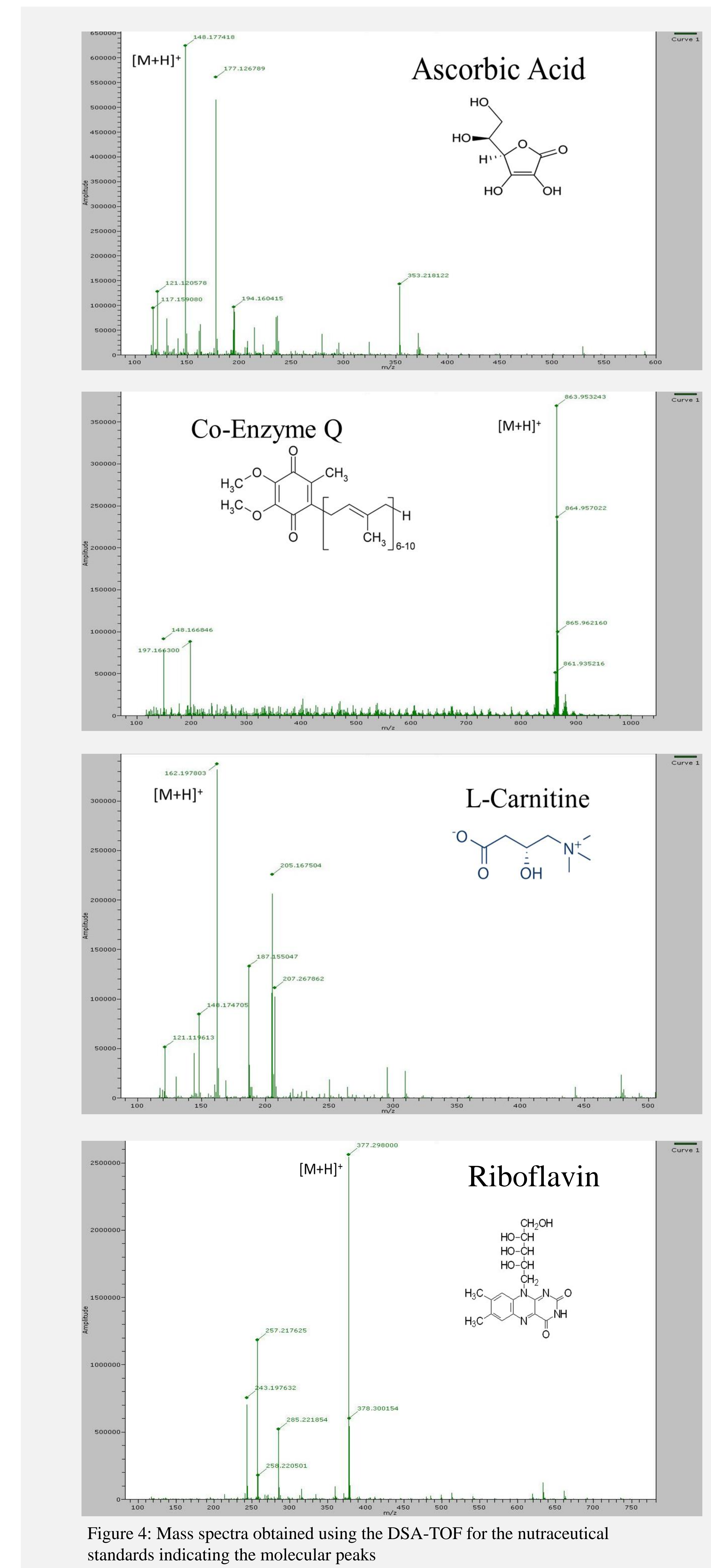
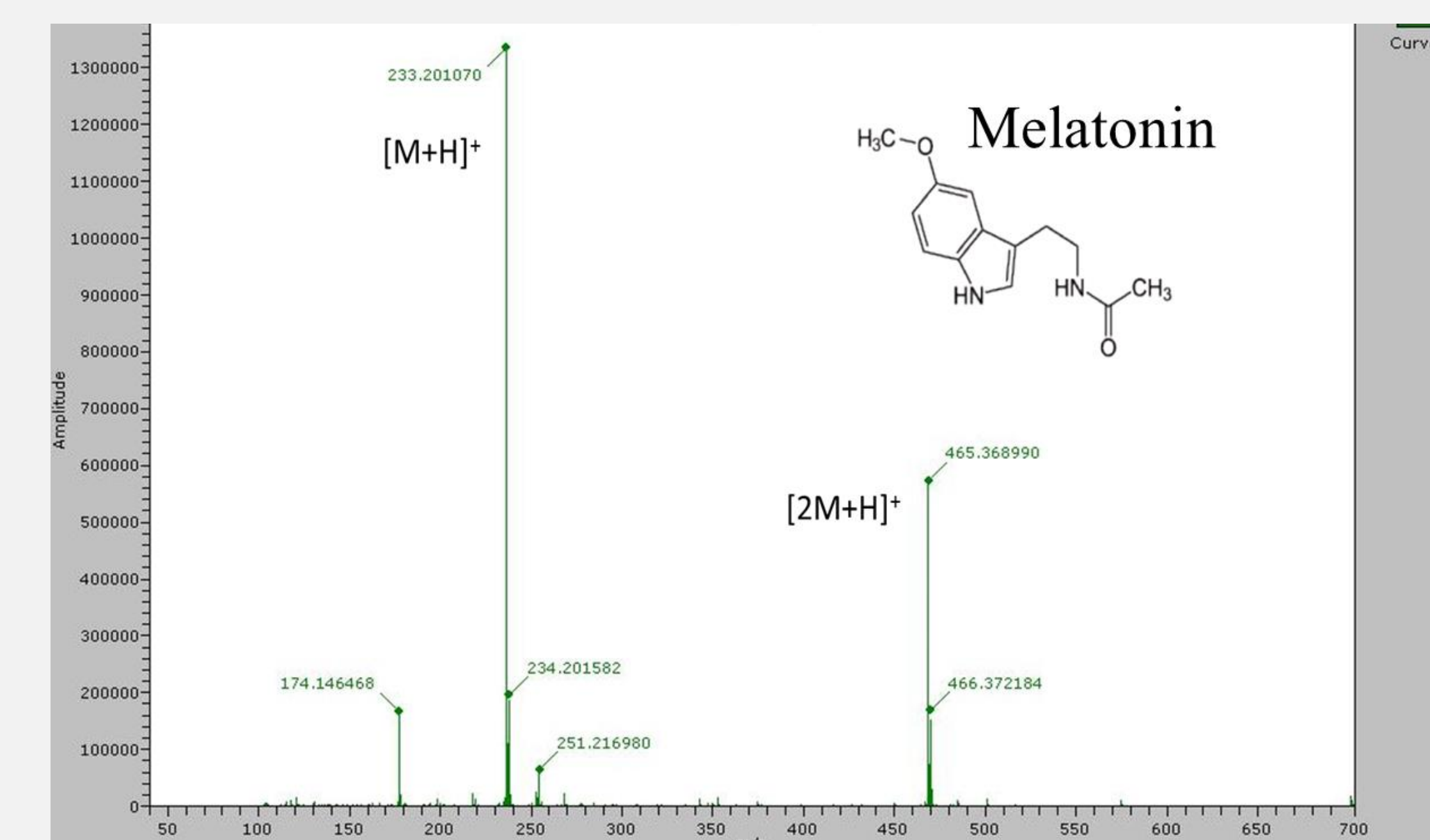


Figure 4: Mass spectra obtained using the DSA-TOF for the nutraceutical standards indicating the molecular peaks

8 Commercial Product Spectra

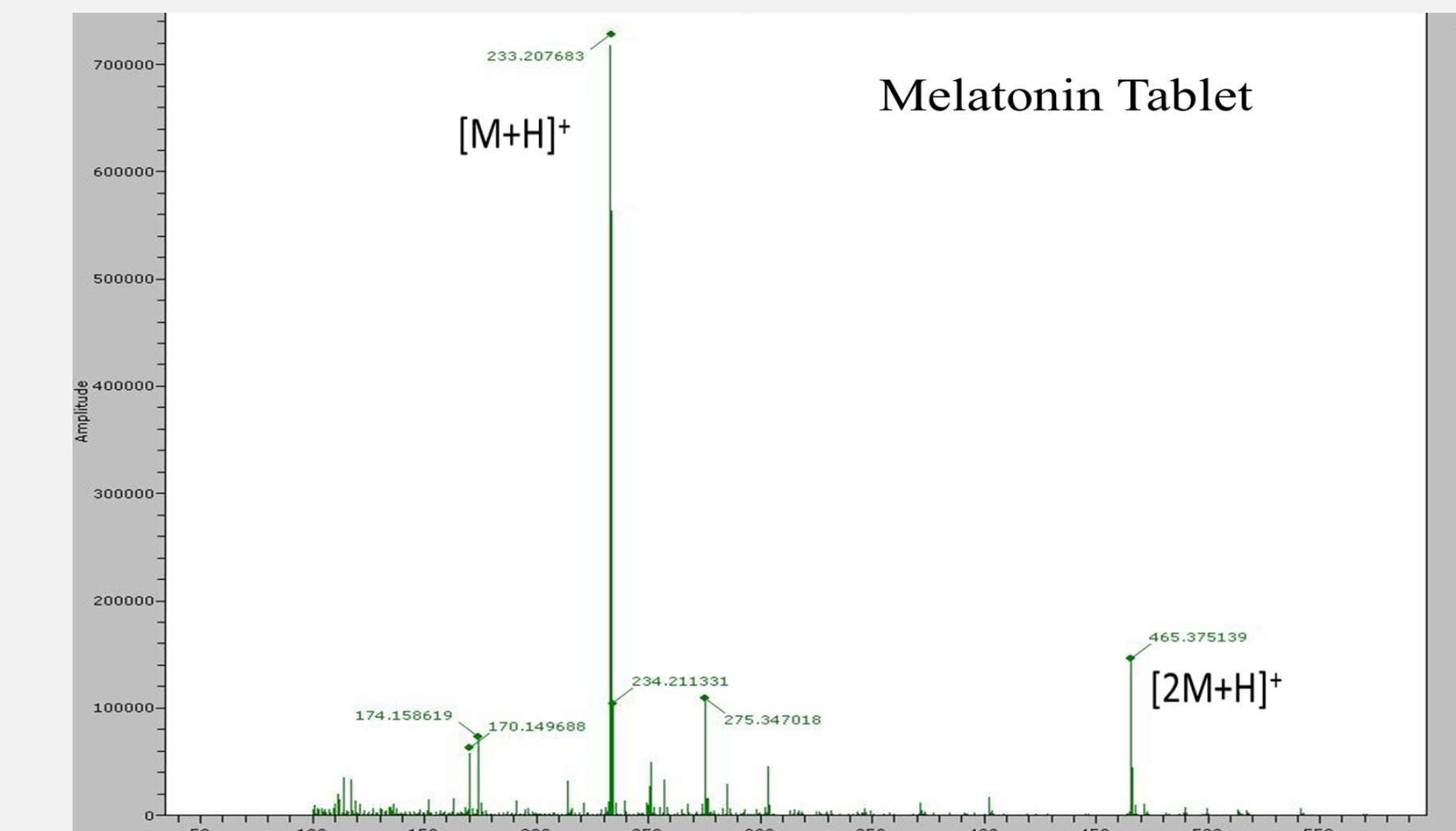


Figure 5: Mass spectra of a 10mg melatonin tablet which was crushed into a fine powder and directly applied to the DSA screen for analysis

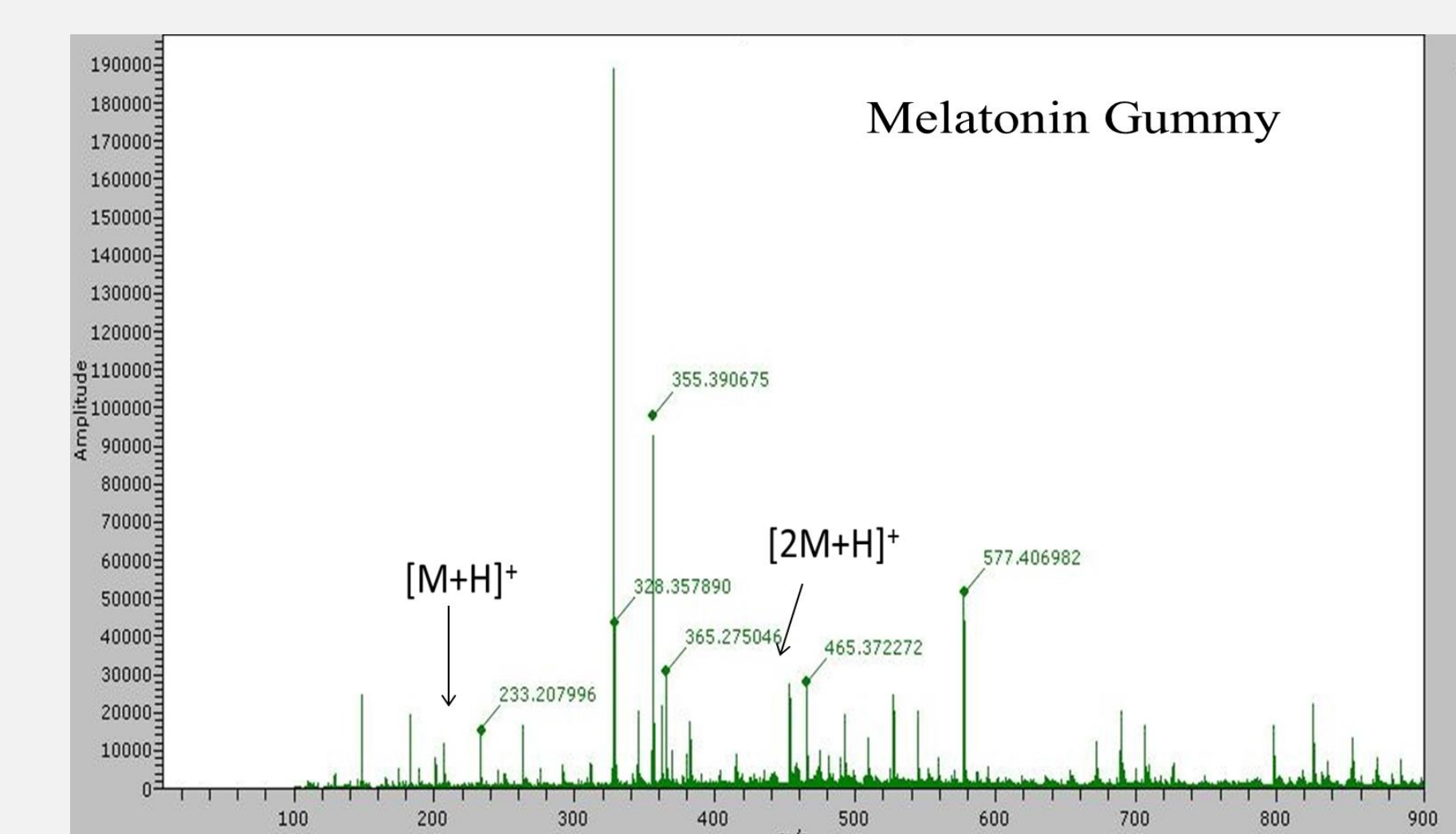


Figure 6: Mass spectra of a flavored melatonin gummy. It was cut in half and rubbed directly on the DSA screen.

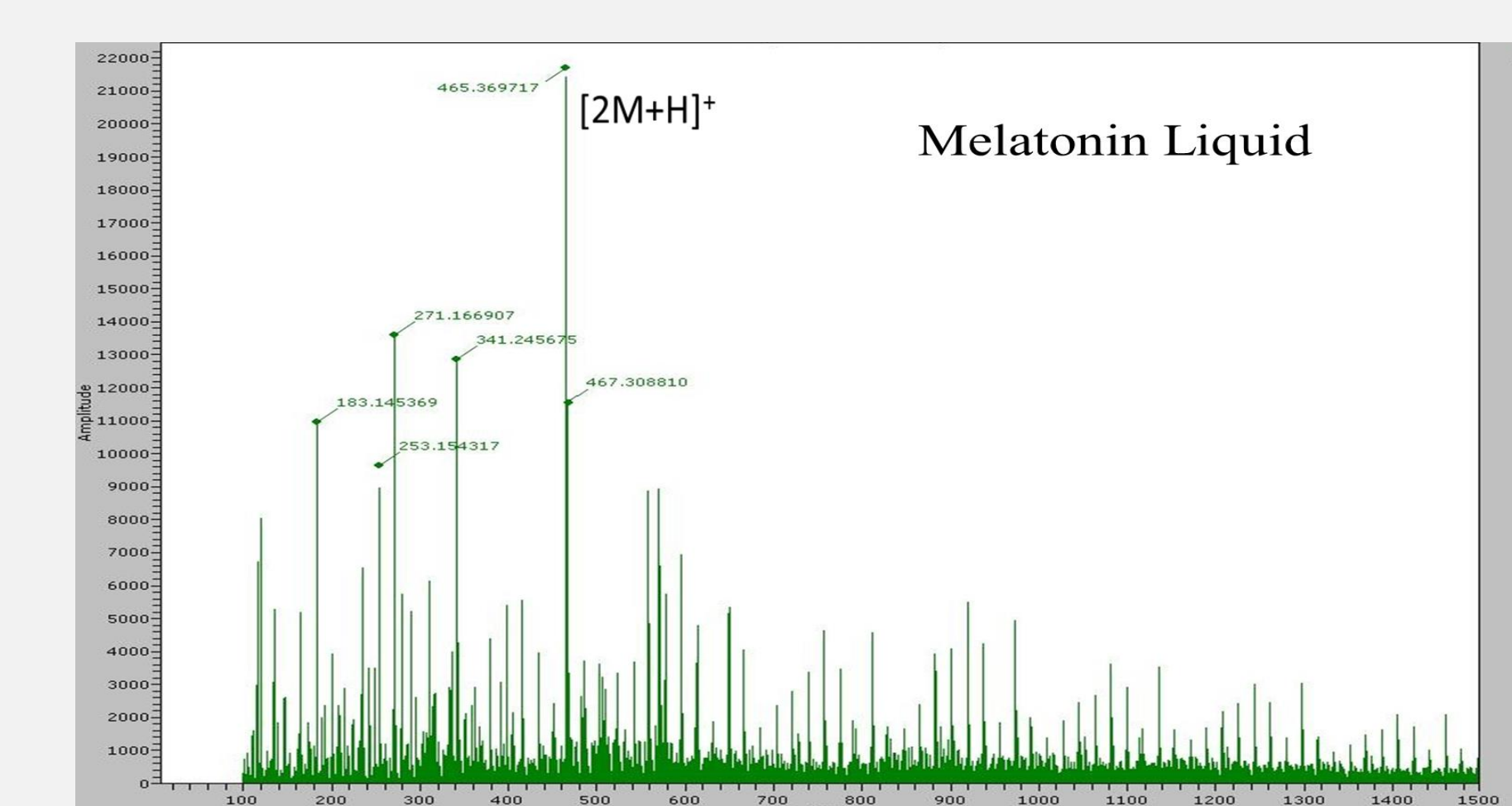


Figure 7: Mass spectra of a flavored melatonin containing liquid applied to the DSA spectra allowed to dry for fifteen minutes.

7 Conclusion

*Direct Sample Analysis coupled with Time of Flight Mass spectrometry allows for the clear detection of nutraceutical molecules in a quick and efficient manner.

*Conditions on DSA-TOF instrumentation were optimized for each nutraceutical standard and produced spectra with strong peak intensities for the desired m/z ratios and showed little additional noise. The detection of molecular peaks of desired nutraceutical compounds in commercially available products indicates that this is an effective method for analysis.

*This research will be continued by analyzing the spectra obtained from DSA-TOF analysis and determining the source of all peaks and matching them with the advertised ingredients; specifically seeking to identify any harmful compounds that may be present.

*Development of a standardized and easily reproducible method for nutraceutical compounds will potentially allow for stricter and more specific regulation of these products as they grow in availability and popularity.

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References : 1 <http://dyadic.com/nutraceuticals> 2 <http://www.nosleeplessnights.com/wp-content/uploads/2013/09/pills-for-kids.jpg> 3 <http://www.americanlaboratory.com> 4 <http://www.chm.bris.ac.uk/ms/theory/tof-masspec.html> 5 PerkinElmer resources for Axion DSA-TOF