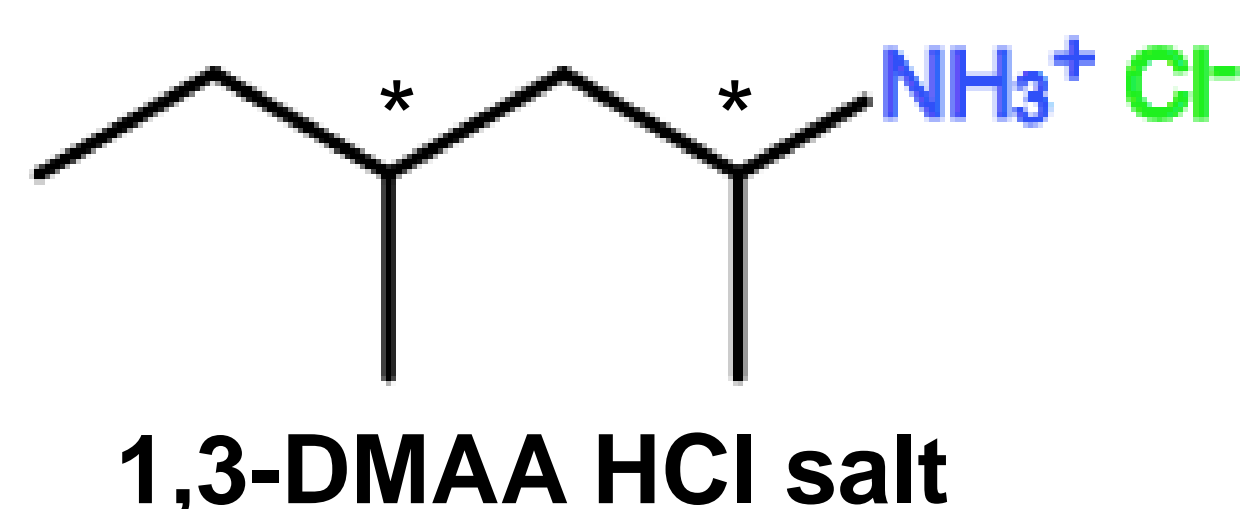
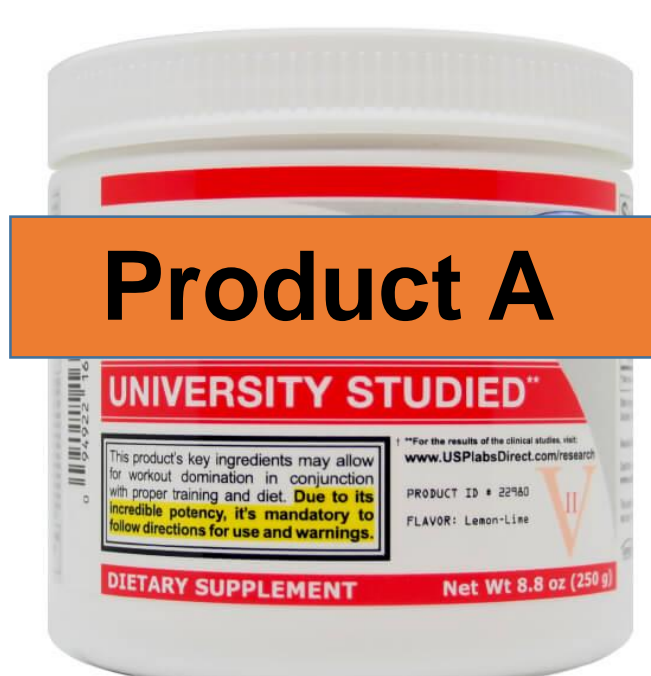


Introduction

The subject compound, 1,3-dimethylamylamine (DMAA), is a “natural” stimulant found in nutritional supplements, weight loss, and athletic performance-enhancing products. This amphetamine-like compound is linked to cardiovascular problems such as shortness of breath, arrhythmias, chest tightness, heart attacks, and multiple deaths [ref 1]. DMAA was banned in 2010 by the International Association of Athletics and the International Olympic Committee which both abide by the policies set forth by the World Anti-Doping Agency [ref 2]. Our laboratory recently developed a quantitative method to determine the presence and amount of DMAA in commercial products by GC-FID and GC-MS.



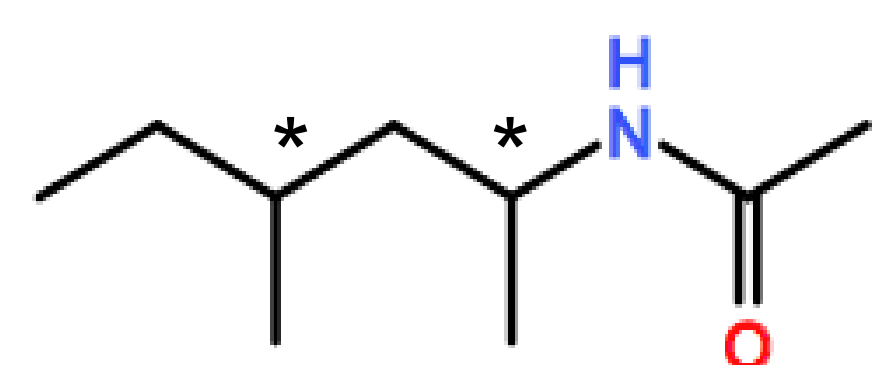
* chiral center

Objectives

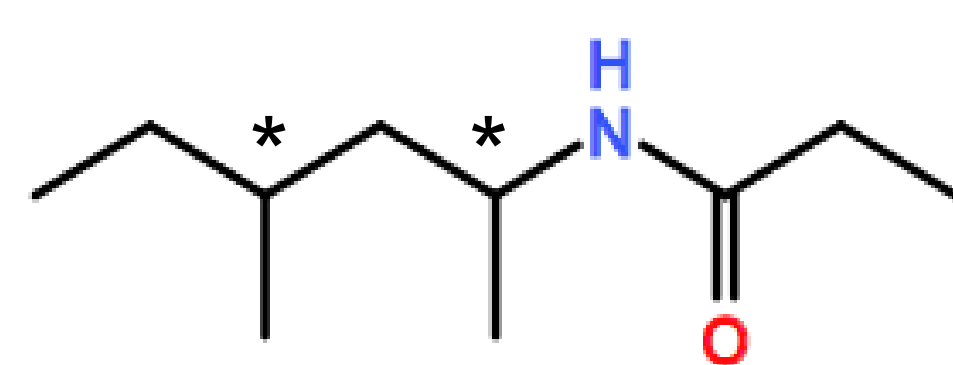
The purpose of this project was to optimize the sensitivity of an existing analytical method to quantitate DMAA via derivatization using alkanolic anhydrides of varying molecular weight.

Experimental

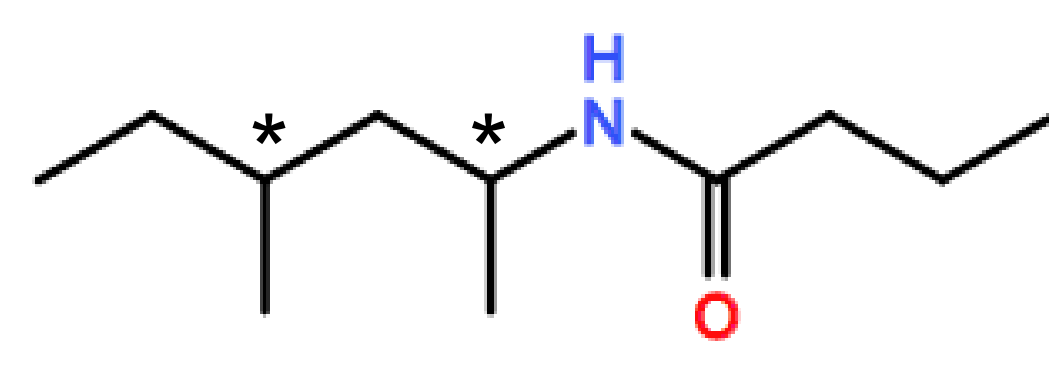
Sample Preparation: DMAA free base and Decane (C₁₀) stock solutions were prepared in CHCl₃ and derivatized with alkanolic anhydrides (acetic, propanoic, and butanoic) to give the corresponding amides. Trimethylamine (TEA) was added to aid in the derivatization (acylation).



DMAA-acetyl amide



DMAA-propanoyl amide



DMAA-butanoyl amide

Analytical Conditions:

- Agilent 7890A GC-FID: Column Rtx – 5ms, 30 m x 0.25 mm x 0.25 mcm load, helium carrier gas flow = 1mL/minute, split flow = 50:1
- Agilent 7890A/5975C GC-MSD: ZB-5 30 m x 0.25 mm x 0.25 mcm load, helium carrier gas flow = 1mL/minute, split flow = 50:1

Results

Quantitation of DMAA with and without Internal Standard

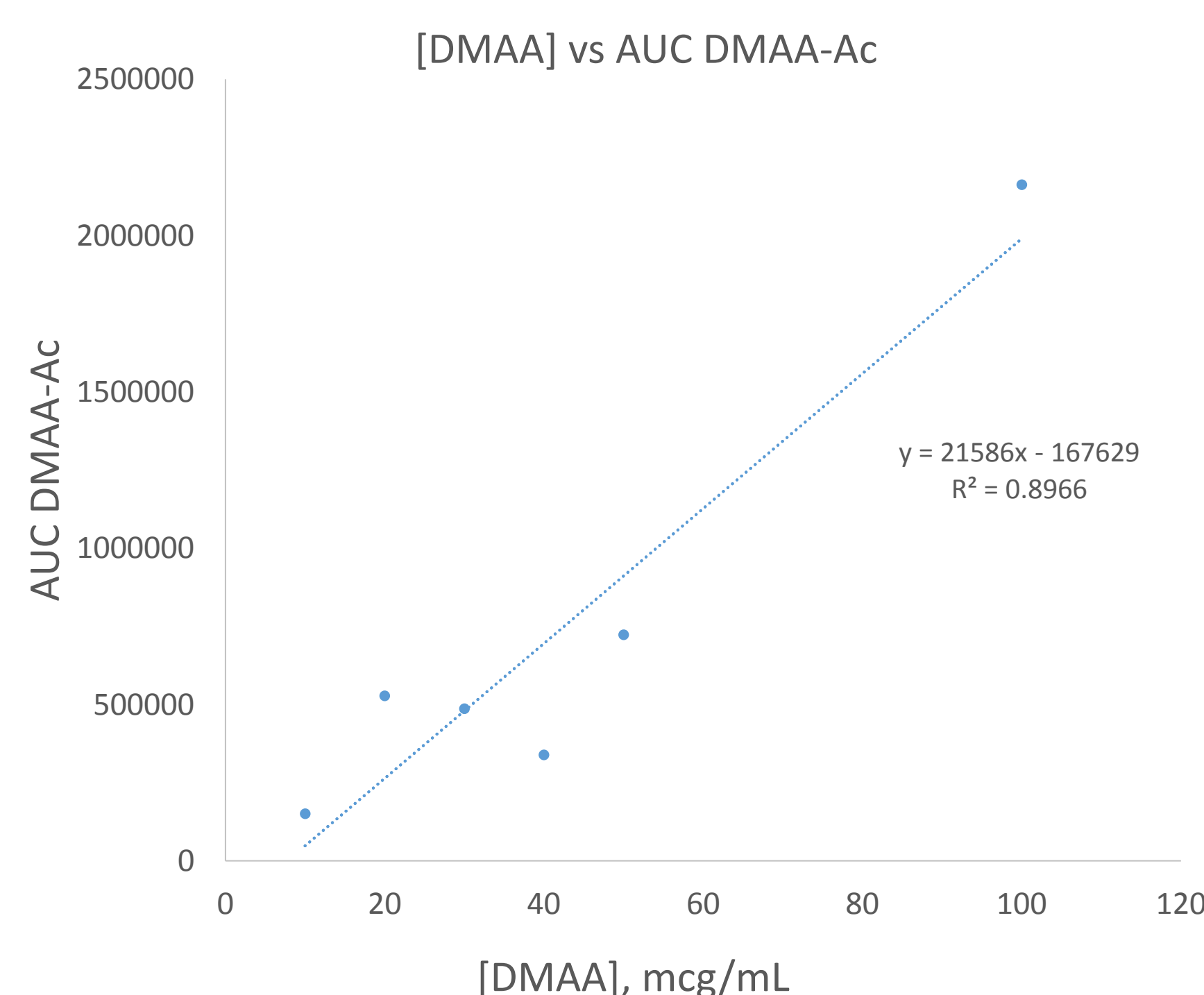


Figure 1: Calibration Curve of GC-FID Response vs [DMAA-Ac] with Internal Standard.

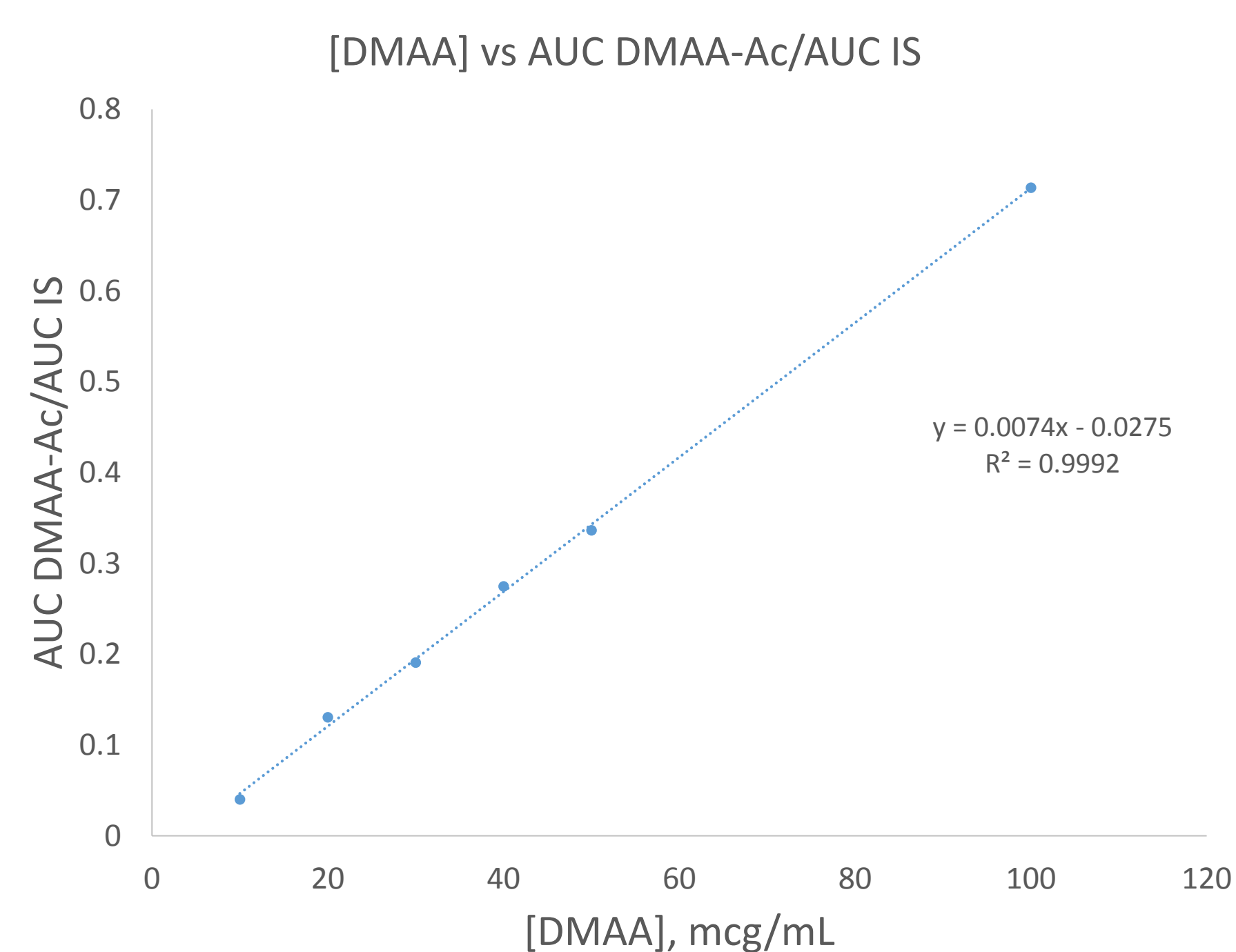


Figure 2: Calibration Curve of GC-FID Response vs [DMAA-Ac] with Internal Standard.

Results (cont'd)

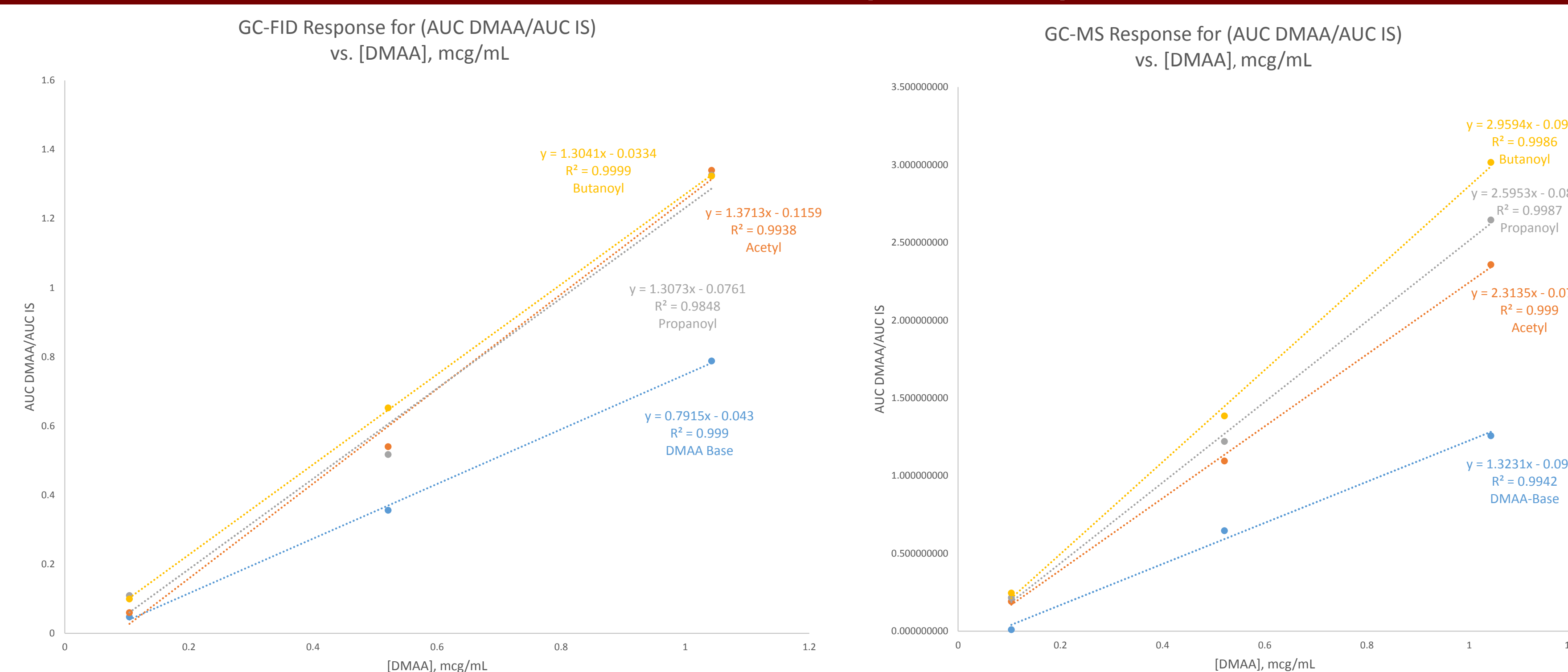


Figure 3: Calibration curves for DMAA-amides by GC-FID and GC-MS

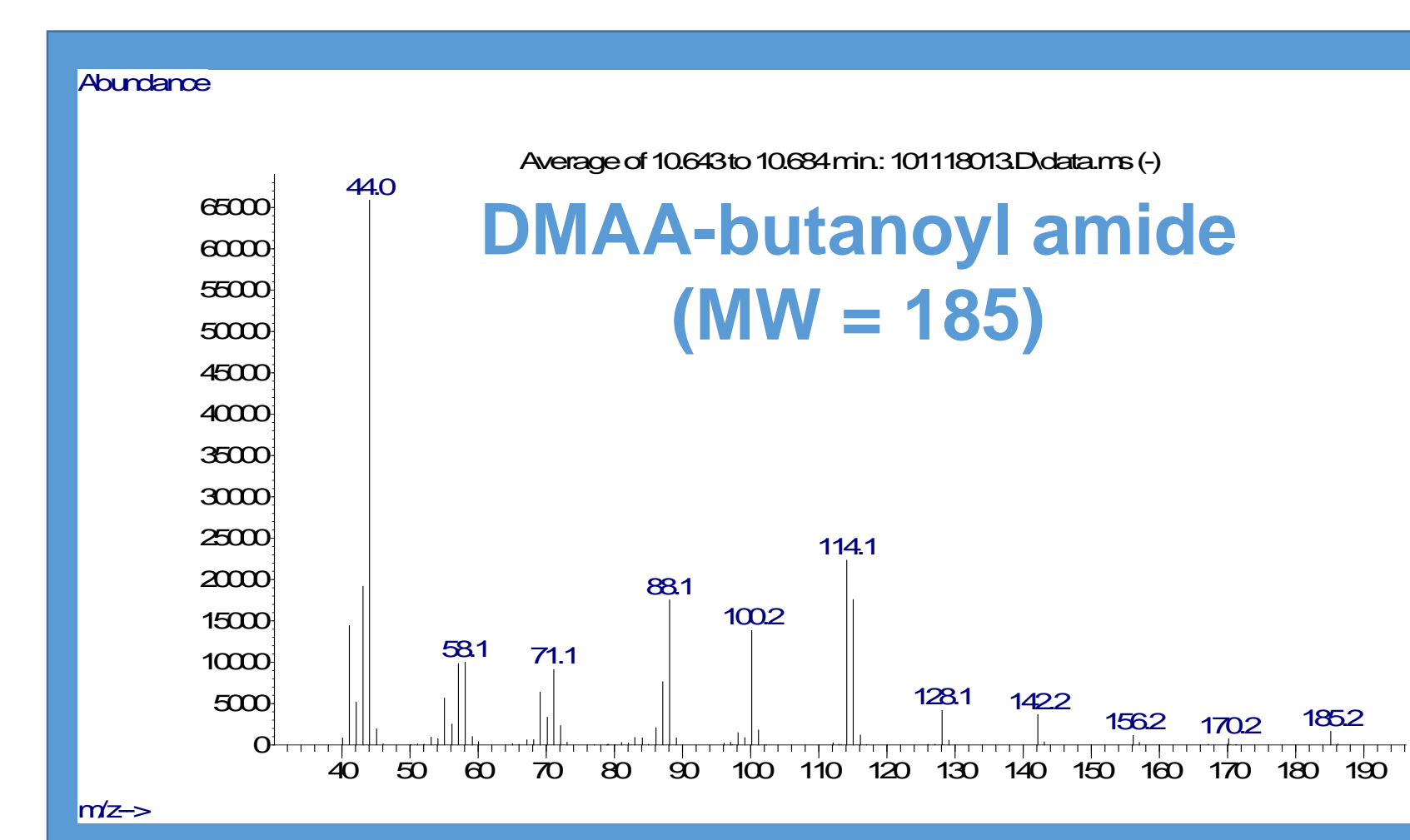
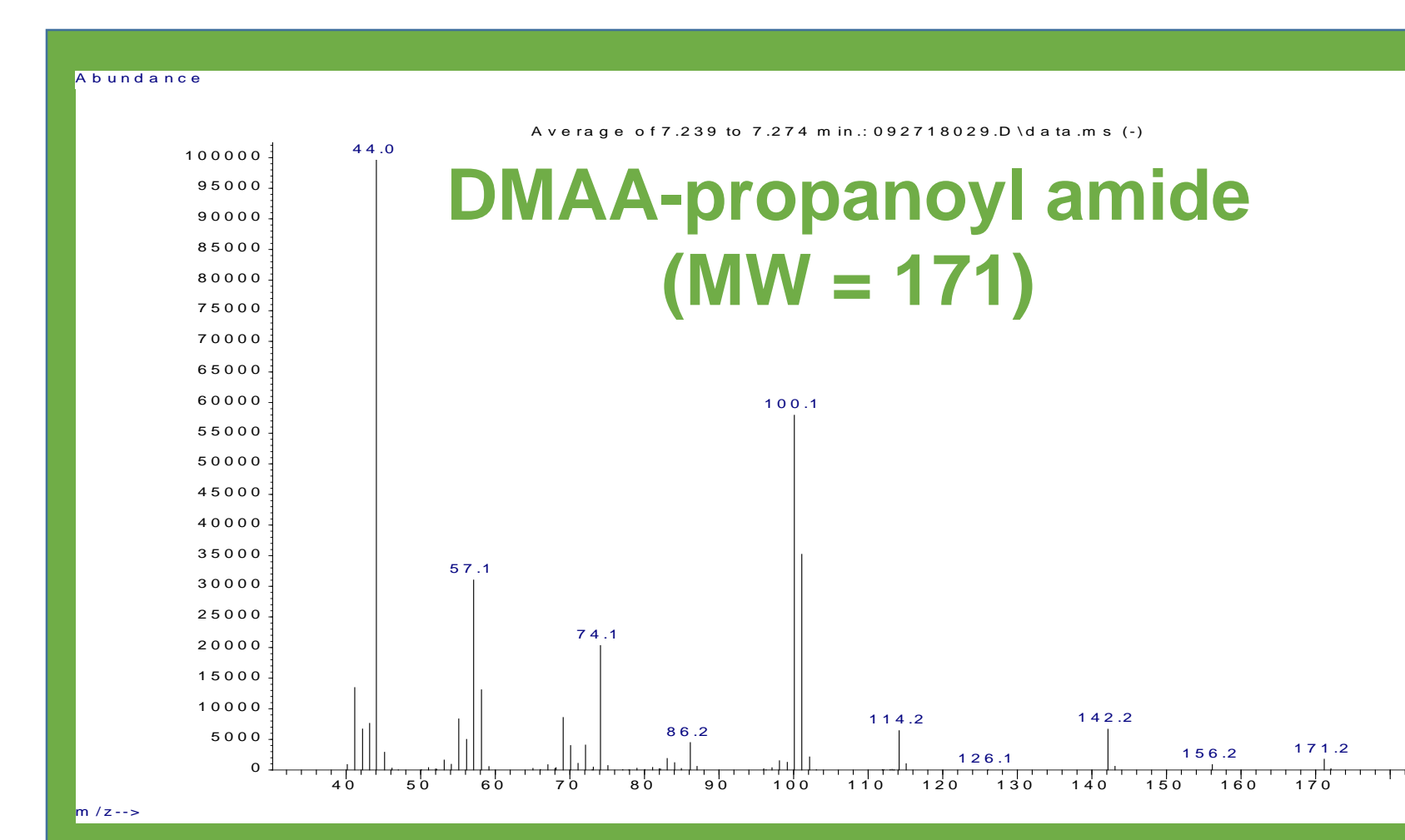
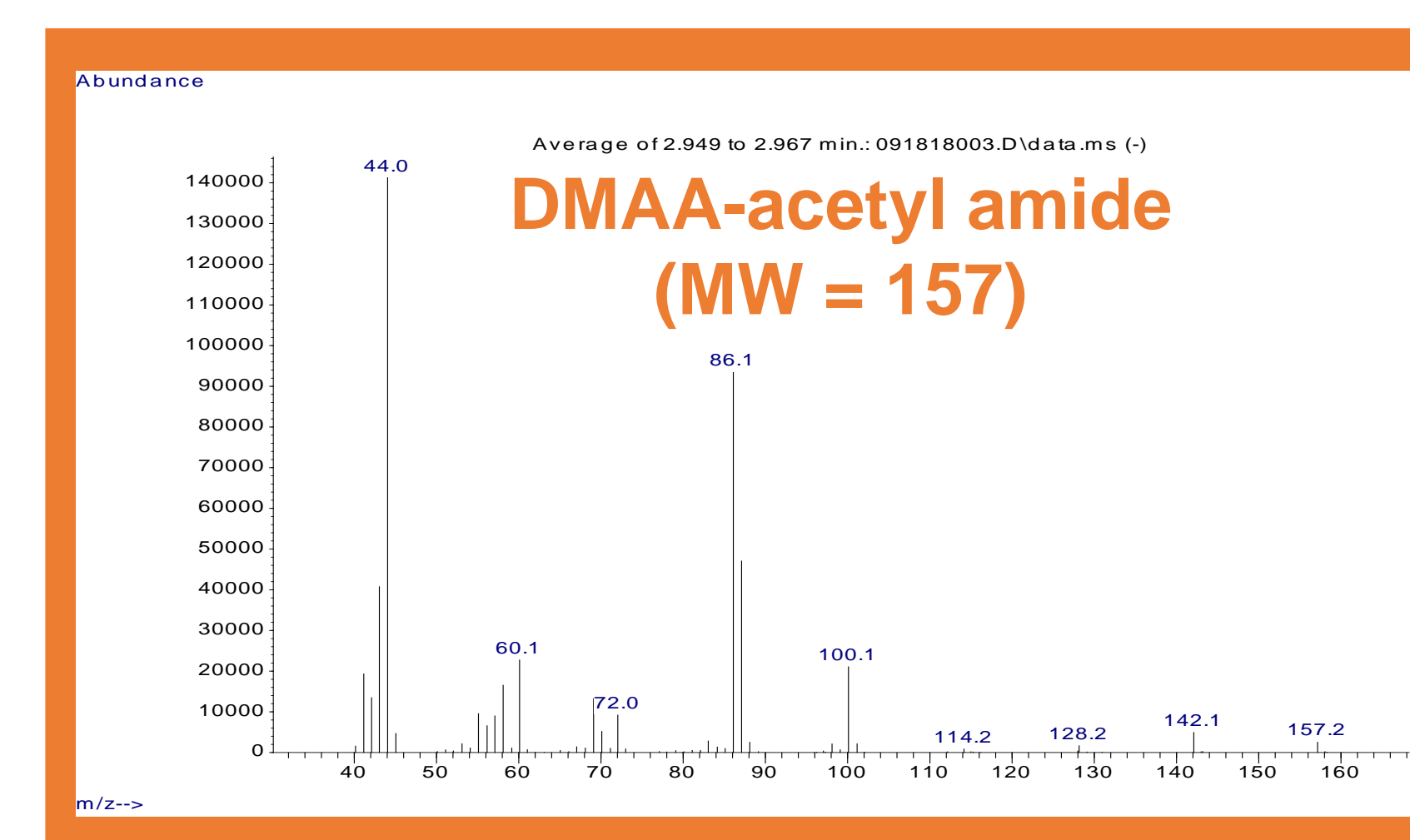
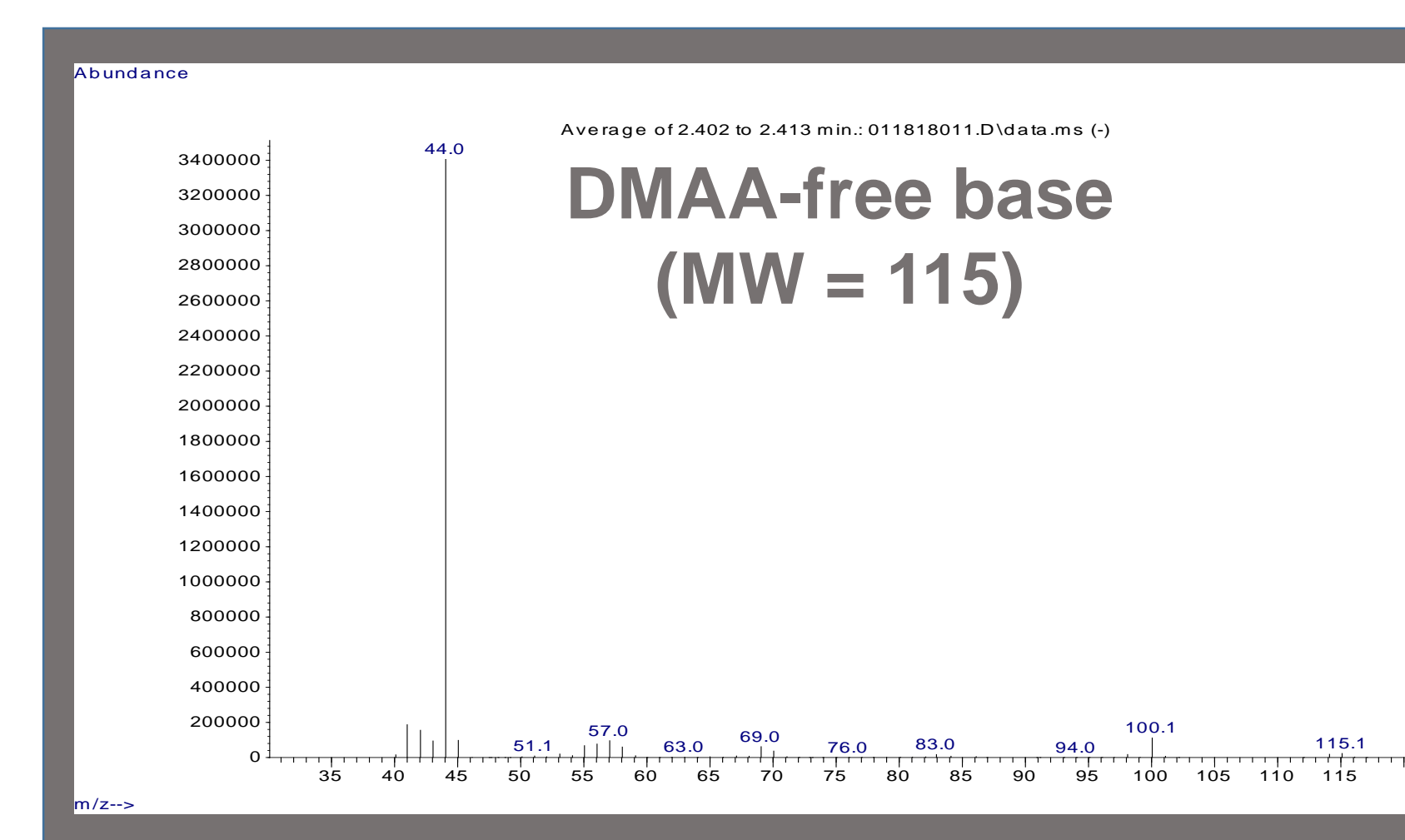


Figure 4: GC-MSD spectra of DMAA-amide derivatives (full scan)

Conclusions/Future Work

- In the quantitation of DMAA derivatized with acetic anhydride, calibration curves showed a marked improvement in fit and linearity with the addition of a Decane Internal Standard (Figs 1 and 2).
- Linear detector response was obtained for derivatives using both detection methods (FID and MSD, Fig 3).
- Sensitivity of the analytical method increased with increasing size of the derivatizing group (base < acetyl < propanoyl < butanoyl) in both FID and MSD detection methods (Fig. 3).
- Future work will focus on maximizing the sensitivity of the MS method by employing lower split values and selective ion monitoring.
- We are grateful to Loyola University Chicago for support of this research project through the Mulcahy Scholarship Program.

References

- Center for Food Safety and Applied Nutrition. “Products & Ingredients - DMAA in Dietary Supplements.” *U S Food and Drug Administration Home Page*, Center for Food Safety and Applied Nutrition, 13 July 2013, www.fda.gov/food/dietarysupplements/productsingredients/ucm346576.htm.
- “The 2010 Prohibited List International Standard.” *World Anti-Doping Agency*, World Anti-Doping Agency, 2010, https://www.wada-ama.org/sites/default/files/resources/files/WADA_Prohibited_List_2010_EN.pdf