



## Young Forensic Scientists Forum— 2019

### Y18 A New Assay for 1,3-Dimethylamylamine: An Emerging Drug of Abuse

Sandra M. Pieczonka\*, Loyola University Chicago, Crystal Lake, IL 60014

**Learning Overview:** After attending this presentation, attendees will be able to understand the dangers of 1,3 Dimethylamylamine (DMAA), learn about techniques that other scientists have used previous to this research, and discover how this research has changed the way this compound can be analyzed using easier methods and more inexpensive materials.

**Impact on the Forensic Science Community:** This presentation will impact the forensic science community by introducing a new way of analyzing banned substances more accurately, more quickly, and more cost effectively.

The subject compound, DMAA, is marketed as a “natural” stimulant in nutritional supplements and is often found in weight loss and athletic performance-enhancing products. Recent studies have linked this amphetamine-like compound to cardiovascular problems such as shortness of breath, tightening in the chest, and possible heart attack. Consumption of DMAA, also known as methylhexanamine, geranamine, and 2-amino-4-methylhexane, has been linked to multiple deaths.<sup>1</sup> This compound was banned in 2010 by competitive sports authorities, such as the International Association of Athletics and the International Olympic Committee, both of which abide by the policies set forth by the World Anti-Doping Agency.<sup>2</sup> Any quantity of DMAA found in an athlete’s urine results in automatic suspension and sanction. In the past few years, DMAA has been identified in seized drug exhibits by the Drug Enforcement Administration (DEA).<sup>3</sup>

Qualitative and quantitative methods previously reported in the literature have used High-Performance Liquid Chromatography/Ultraviolet (HPLC/UV), Proton Nuclear Magnetic Resonance (<sup>1</sup>HNMR), Mass Spectrometry (MS), and Gas Chromatography (GC).<sup>4-7</sup> This new method uses GC/MS and Flame Ionization Detection (FID) to assay DMAA in commercial products, usually in the form of the hydrochloride salt (DMAA.HCl). Sample preparation consists of extracting DMAA.HCl with aqueous HCl in the range of 0.1M–0.5M followed by conversion of DMAA.HCl to the free base with aqueous sodium hydroxide (NaOH) solution and extraction into chloroform. On-column derivatization to the DMAA-alkanoyl amide was achieved in chloroform with the addition of a lower alkanoyl anhydride and triethylamine. Compared to the free base, DMAA-acyl amide derivatives have increased volatility and decreased surface activity, which results in enhanced chromatography, detector response, and specificity. Additionally, this new method does not require heating or sonication prior to analysis and uses readily available laboratory chemicals for derivatization, such as acetic, propanoic, and butanoic anhydrides. The use of various alkanoyl anhydrides provides method versatility across a broad product line and avoids interference from components in certain commercial products. Acylation of DMAA with a homologous series of anhydrides creates amides with predictably later retention times. Lastly, the resolution of the diastereomeric analyte pairs was enhanced as the molecular weight of the derivatizing agent increased.

#### Reference(s):

1. 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](http://www.fda.gov/food/dietarysupplements/productsingredients/ucm346576.htm).
2. 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](https://www.wada-ama.org/sites/default/files/resources/files/WADA_Prohibited_List_2010_EN.pdf).
3. DEA Emerging Threat Reports, 2016-2018, Special Testing and Research Laboratory. <https://ndews.umd.edu/resources/dea-emerging-threat-reports>.
4. Fleming, Heather L. et al. Analysis and Confirmation of 1,3-DMAA and 1,4-DMAA in Geranium Plants Using High Performance Liquid Chromatography with Tandem Mass Spectrometry at Ng/g Concentrations. *Analytical Chemistry Insights*, Libertas Academica, 8 Nov. 2012. [www.ncbi.nlm.nih.gov/pmc/articles/PMC3512447/](http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3512447/).
5. Monakhova, Y.B. et al. Rapid Assessment of the Illegal Presence of 1,3-Dimethylamylamine (DMAA) in Sports Nutrition and Dietary Supplements Using <sup>1</sup>H NMR Spectroscopy. *Drug Testing and Analysis*, U.S. National Library of Medicine, Sept. 2014. [www.ncbi.nlm.nih.gov/pubmed/24913715](http://www.ncbi.nlm.nih.gov/pubmed/24913715).
6. Lesiak, A.D. et al. DART-MS for Rapid, Preliminary Screening of Urine for DMAA. *Drug Testing and Analysis*, U.S. National Library of Medicine, 25 Oct. 2013. [www.ncbi.nlm.nih.gov/pubmed/24167149](http://www.ncbi.nlm.nih.gov/pubmed/24167149).
7. Zhang Y.; Woods, R.M.; Breitbach, Z.S.; Armstrong D.W. 1,3-Dimethylamylamine (DMAA) in Supplements and Geranium Products: Natural or Synthetic? *Drug Test. Analysis* 2012, 4, 986-990.

#### 1,3-dimethylamylamine, DMAA, Assay