E95 I Smell a Rat: Optimizing a Method for Detecting the Rat Poison Brodifacoum With Gas Chromatography

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Learning Overview: After attending this presentation, attendees will understand how to detect brodifacoum, a type of rat poison that has recently gained notoriety as an emergent adulterant to illicitly purchased controlled substances, using Gas Chromatography/Mass Spectrometry (GC/MS) and Gas Chromatography with Flame Ionization Detection (GC/FID). It is imperative that both GC/MS and GC/FID, two gold standards within the field of forensic chemistry, are capable of detecting this lethal compound. A method for detecting brodifacoum will be discussed by varying several instrument parameters (e.g., column length and inlet temperature). As proof of principle, the optimized method will then be applied to mock case samples.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by providing a validated method to target this emergent adulterant. Forensic methods often trade run time by sacrificing detection of these later-eluting compounds. Such rapid schemes run at odds of assessing the potential presence of brodifacoum. Further, there is a paucity of modern literature to detail the analytical detection of this compound, or even related compounds, via GC. Thus, available methods discussed in literature are not germane to current analytical instrumentation.

Brodifacoum is currently a common rodenticide belonging to the class of pesticides known as "superwarfarins." These compounds were developed from toxicants of warfarin, a response to the increase in warfarin-resistant rats and mice. Brodifacoum is a coumarin anticoagulant, causing hemorrhaging and severe vitamin K deficiency after prolonged exposure. It has the potential to be lethal both to rodents and to humans due to its long half-life and, thus, residency within the body.[1]

In early 2018, Illinois health care providers reported multiple cases of patients with unexplained bleeding who had also self-reported as using illicit substances, specifically synthetic cannabinoids. Further clinical testing detected the presence of brodifacoum as a likely causative factor in hemorrhaging, which was later found to be present in tested synthetic cannabinoid samples.[2] Over the following months, more than 200 clinical cases of brodifacoum poisoning resulting from synthetic cannabinoid use were reported in nine states.[3] While exposure to brodifacoum is only seldom lethal, the treatment is prolonged and requires hospitalization.[4]

In Washington, DC, the use of synthetic cannabinoids has significantly escalated since 2015. For example, over a two-week peak period in July 2018, DC Fire and Emergency Medical Services (EMS) reported more than 450 calls for suspected synthetic cannabinoid overdoses, including some resulting in fatalities.[5] It is imperative that forensic science laboratories in the region and other cities across the country are equipped with optimal methods for detecting brodifacoum. Such detection techniques will better equip local public health officials with the tools to detect this toxic compound, as well as other poisons, as these emerge in the local illicit controlled substances.

This research is directed at solving not just a validation scheme, but also to provide the forensic chemist a method to be used on real-world samples. Initial analyses were performed using a sample of brodifacoum in various solvents. Different methods and different column lengths were tested using both GC/MS and GC/FID. Additionally, the inlet temperature was adjusted to account for any possible thermal decomposition of brodifacoum. Once optimal parameters were established, non-controlled plant material was adulterated with brodifacoum, synthetic cannabinoids, and various combinations of both in order to mimic real-world scenarios. Further analyses will seek to establish the optimal method for detecting brodifacoum and other similar rodenticides in combination with common spices and controlled substances.

The initial screen for brodifacoum in acetone using GC/MS produced two late eluting peaks; these results were consistent for all methods and column lengths tested. The results were also repeatable when analyses were conducted in a variety of solvents. An observed decrease in peak area indicated that inlet temperatures greater than 260°C resulted in the breakdown of brodifacoum. When analyzed with GC/FID, two late eluting peaks were also present. The results of both GC/MS and GC/FID will be compared to determine which approach is optimal for detecting trace amounts of brodifacoum, but additionally, both instruments will be demonstrated to function to successfully presumptively detect and confirm the presence of brodifacoum in samples, a requirement for confirmation under the Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) guidelines.

Reference(s):

1. Douglas Feinstein, Sergey Brodsky, Guy Weinberg, Richard van Breeman, and Israel Rubinstein. Brodifacoum Poisoning: A Clear and Present Danger to Public Health in the USA. *Toxicology Letters*, no. 268 (2017): 71-72.
2. Erin Moritz et al, Notes from the Field: Outbreak of Severe Illness Linked to the Vitamin K Antagonist Brodifacoum and Use of Synthetic Cannabinoids—Illinois, March–April 2018. *Center for Disease Control and Prevention Morbidity and Mortality Weekly Report*, no. 21 (June 1, 2018): 607-608.
3. Cascade City Health Department. *Outbreak of Life-Threatening Coagulopathy Associated with Synthetic Cannabinoids Use.* City County Health Department & Community Health Care Center, Inc., last modified May 30, 2018.
4. Indiana State Department of Health. *Synthetic Marijuana Linked to Cases of Severe Bleeding in Illinois and Indiana*. Indiana Health Alert Network Advisory, last modified March 28, 2018.
5. Marisa Peñaloza. D.C. Has Had More Than 300 Synthetic Marijuana Overdoses in 2 Weeks. *National Public Radio*, last modified July 27, 2018.

Brodifacoum, Synthetic Cannabinoids, Gas Chromatography