LC/MS/MS Analysis of Biogenic Amines in Foods and Beverages

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Biogenic amines are a group of biologically active organic compounds produced by decarboxylation of free amino acids. They are found in bacterially contaminated food, particularly in fish and are therefore potential quality indicators. They can, in sufficient concentrations, pose a threat to human health. Histamine is the main causative agent in Scombroid fish poisoning. The other biogenic amines such as putrescine, cadaverine and tyramine are also of great interest as their presence enhances the toxicity of histamine. Biogenic amines can also react with nitrites to form potentially carcinogenic nitrosamines. Analysis of these amines is usually carried out by ELISA at a detection limit of low – medium ppm. Analysis by traditional RP-HPLC is difficult because of poor retention. Derivatization methods are time consuming, ion-pairing agents can inhibit LC/MS analyses, and both can adversely affect method reproducibility. In 2006 we investigated the use of cation-exchange column coupled with tandem mass spectrometry detection to analyze biogenic amines in seafood. Although the method worked well, it requires column regeneration, ion suppressor, etc., and is not suited for high throughput analysis. With the introduction of new LC phases, we wanted to see if HILIC or fluorinated packing material can handle the direct analysis of these polar biogenic amines: cadaverine, histamine, 2-phenylethylamine, putrescene, serotonin, spermidine, spermine, tryptophan, tryptamine, tyramine and urocanic acid. We examined several LC columns and found that Pinnacle® DB PFPP works fine with 0.05% trifluoroacetic acid for all of these amines with detection limits (based on S/N=10) of low ppb. The current Food Standards Code indicates the permitted level for histamines to be 200 mg/Kg or 200 ppm. Therefore, our new method meets the requirement for routine screening for these compounds. m, 150 x 2.1 mm PFPP column requires 12 minutes or less per sample.µThe analysis time including column regeneration is 6 minutes using a 1.9-um, 50 x 2.1 mm PFPP column, whereas 5- Over 200 various foods and beverages have been tested in triplicate injections for reproducibility and robustness of this new method. This method was also applied to a study of time, storage condition and concentration of these biogenic amines.

Keywords: biogenic amines, LC/MS/MS, fish