Targeted GC/MS Analysis of Volatile Compounds Relating to Seafood Decomposition

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Abstract

Decomposition in seafood products in the U.S. is monitored by FDA laboratories using sensory testing, which requires highly trained analysts. A large-volume headspace (HS) gas chromatography/mass spectrometry (GC/MS) approach was developed to generate analytical results that can be directly compared to sensory evaluation. A Selected Ion Monitoring (SIM) acquisition method was used to monitor 42 volatile compounds associated with seafood quality changes. Samples of sockeye salmon, yellowfin tuna, mahi-mahi, and black tiger shrimp that have been assessed by an FDA National Seafood Sensory Expert (NSSE) were used for method performance evaluation. Preliminary results determined that chemical quality indices varied among different types of seafood at four stages of decomposition; the large-volume HS-GC/MS-SIM method could be a complementary screening tool to sensory analysis. Key characteristic compounds in headspace volatiles were also tentatively identified.

Introduction

The objectives of this research were threefold:

- To reduce sampling bias by using a 1-L headspace vial which has a higher capacity than a regular headspace vial (6-27 mL).
- To analyze a variety of aroma compounds recovered at the same distribution as experienced by the sensory analyst.
- To analyze four types of seafood products with the established HS-GC/MS-SIM method for 42 different chemical indicators and directly compare the results with FDA sensory evaluation scores.

Materials and Methods

Samples of individually sealed, frozen and unprocessed edible portions for the species of interest have been evaluated by a NSSE. Increments of olfactory assessments were between 0 and 10. Increments between 0 and 4 are considered to be passing and increments between 5 and 10 are considered to be failing (decomposed). All samples were stored at -60 °C prior to analysis.

Agilent 7890B/5975C GC/MS system equipped with the Entech 7650HS-CTS autosampler was used to perform large-volume static headspace GC/MS analysis of volatiles. A portion of 50.0 ± 0.1 g ground seafood and 35.0 ± 0.1 g Na_2SO_4 were added to a 1-L glass headspace vial. Each vial was incubated at 30 °C for 30 min with agitation. Then, a 50 µL of headspace vapor was withdrawn and subject to GC/MS-SIM analysis.

The GC temperature program was as follows: 27 °C, hold for 7 min; ramp at 15 °C/min to 250 °C; ramp at 100 °C/min to 300 °C, hold for 5 min. The injector temperature was 260 °C. The carrier gas (helium, 99.99% purity) flow rate was 1 mL/min constantly. The solvent cut time was 5.8 min. The interface temperature was 260 °C. The MS ion source temperature was 250 °C.

Results and Discussion

Preliminary results determined that chemical quality indices varied among different types of seafood at four stages of decomposition. This result agrees with previous experimental findings in that different compounds play a role in decomposition for different seafood types. Thus, segregation of seafood types is necessary in the analysis of seafood decomposition.

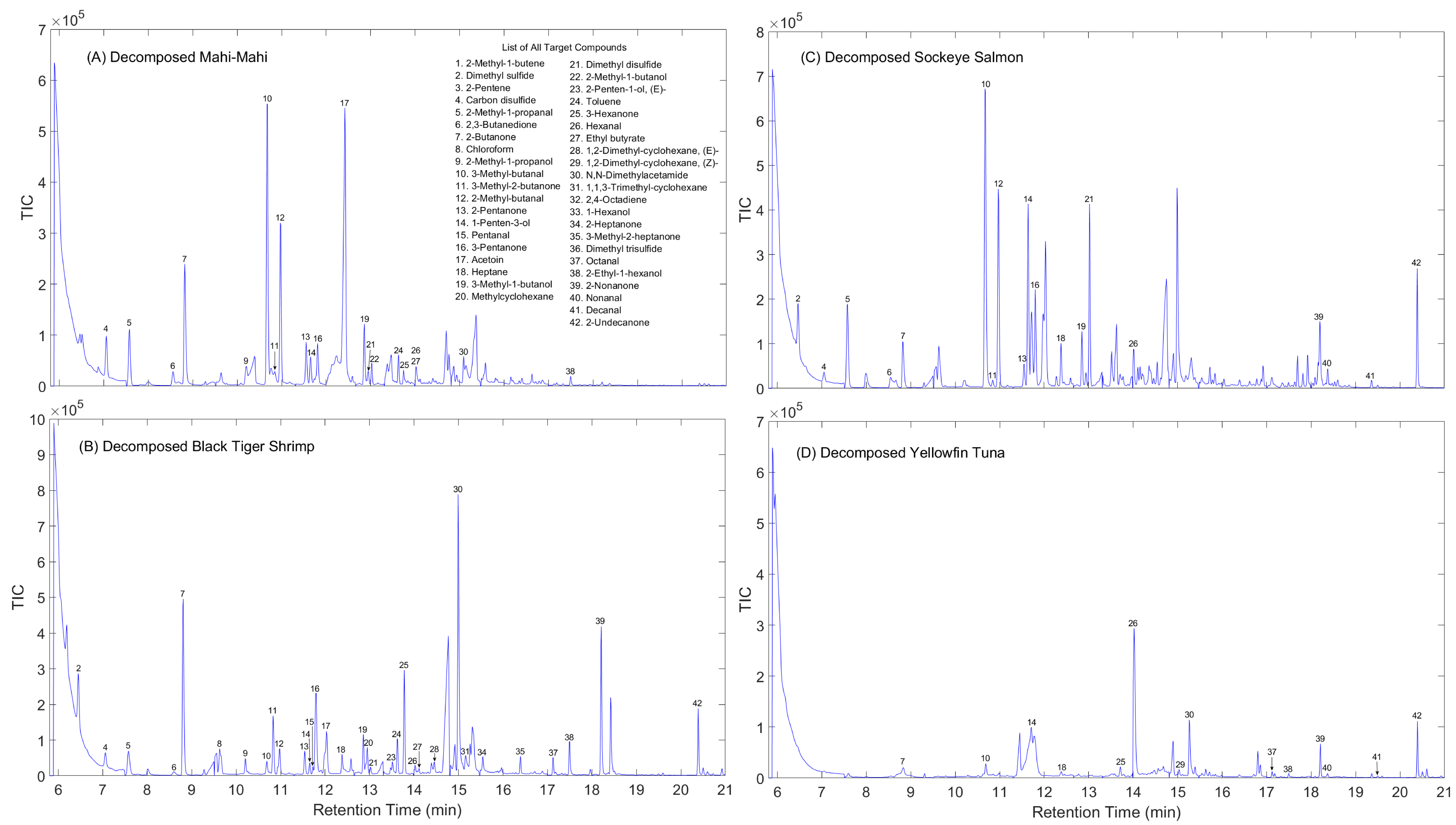
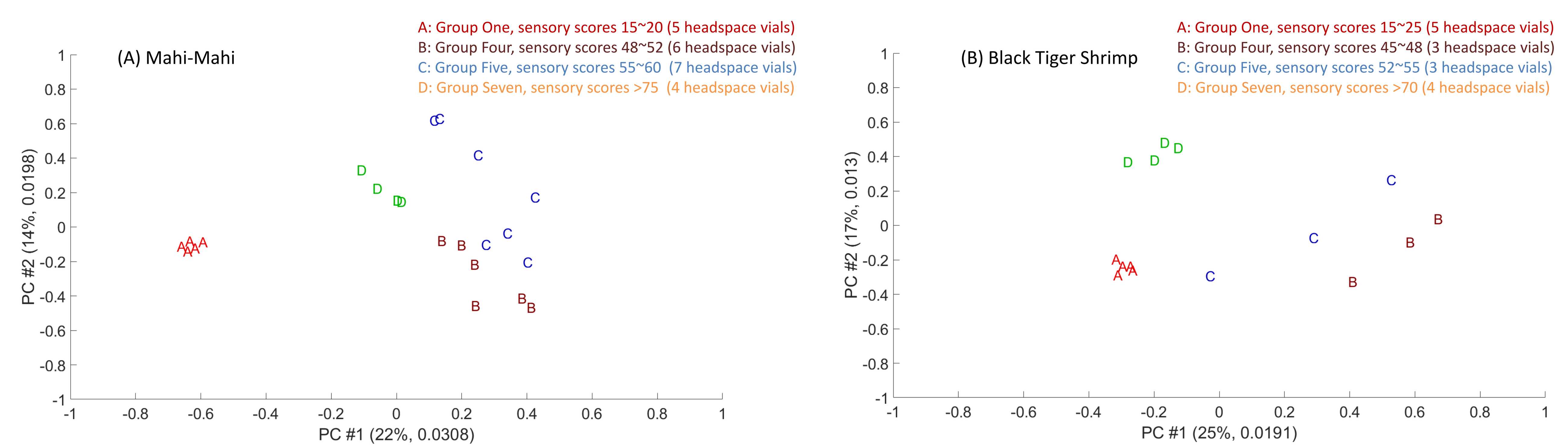


Figure 1. TICs of decomposed (A) mahi-mahi, (B) black tiger shrimp, (C) sockeye salmon, and (D) yellowfin tuna. Chemical profiles were collected using the established large-volume HS-GC/MS-SIM method.

The established method proved to be effective in detecting the 42 target volatile compounds. It was noted that the diversity of seafood caused obvious variations in their headspace chemical compositions. Even though the chemical profiles of the fish species were considerably different, the established large-volume HS-GC/MS-SIM method was sensitive enough to detect the differences.



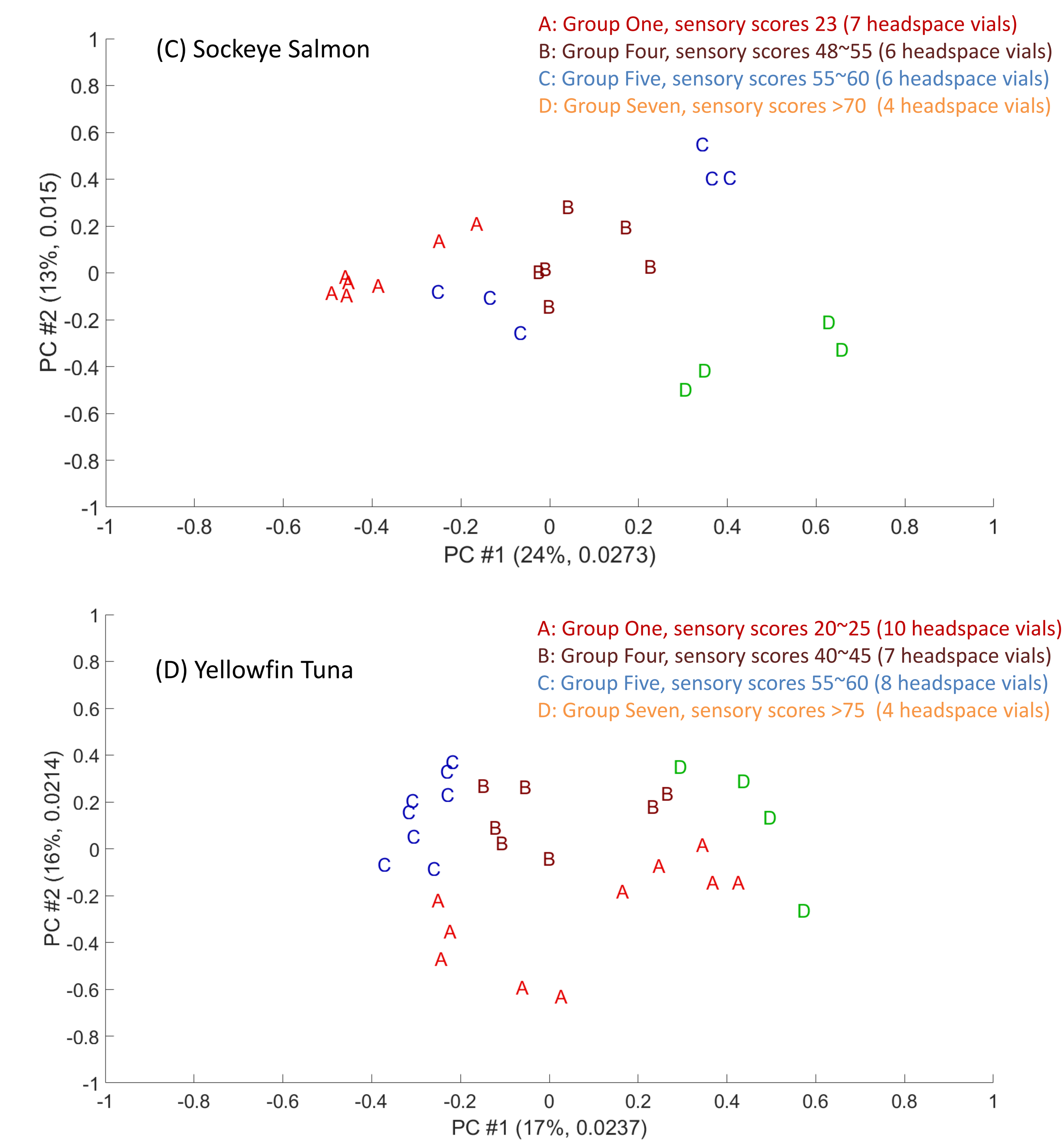


Figure 2. Separability of the GC/MS data sets of (A) mahi-mahi, (B) black tiger shrimp, (C) sockeye salmon, and (D) yellowfin tuna samples at different decomposition stages on the PCA score plots.

Lastly, potential marker compounds for each species were found.

- Mahi-mahi: carbon disulfide, 2-methyl-1-propanal, 2-butanone, 2-methyl-propanol, and hexanal;
- Black tiger shrimp: dimethyl sulfide, 2-butanone, 1-penten-3-ol, and methylcyclohexane;
- Sockeye salmon: 2-methyl-1-propanal, 3-methyl-2-butanone, 2-methyl-butanal, 3-pentanone, dimethyl disulfide, 2-nonanone, and nonanal;
- Yellowfin tuna: 2-butanone, 1,2-dimethyl-cyclohexane, and 2-undecanone.

Conclusion

- ✓ This established large-volume HS-GC/MS-SIM method is applicable for four different types of seafood.
- ✓ Fresh seafood (increment 1) and decomposed seafood (increment 7) can be completely separated.
- ✓ Differentiation of barely acceptable seafood (increment 4) and slightly decomposed seafood (increment 5) is still challenging.
- ✓ Through this technique, potential marker compounds were identified that will be investigated in future studies.
- ✓ The investigation of 42 target volatile compounds indicative of seafood decomposition with large-volume HS-GC/MS-SIM could promisingly support the FDA's seafood sensory program.