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AK-PHL ID: CHEM190213

Topic: Shismaref Smelt

Analytical Chemistry Report

Requesting Organizations: Department of Environmental Conservation – State Veternarian

Contact: Dr. Bob Gerlach Phone: 907-375-8200

Date Received: 02/13/2019

Description: Smelt Fishes from Shishmaref possibly associated with illness. Original submitter noted an off-flavor and undesirable odor—described as exhaust-like, oily, and chemical. Organoleptic Evaluation was conducted by DEC Lab. That evaluation yielded a passing result.

Requested Determination: Test for Dimethyl Sulfide.

Results

1) Surface wipe of fish was non-detect for BTEX, Carbon Disulfide, Dimethyl Sulfide and related small molecule sulfides.
2) Macerated fish muscle contained trace amounts of Carbon Disulfide and a C2- Sulfide compound (Dimethyl Sulfide or Ethyl Mercaptan). It is unknown if the amounts observed are normally present.

Volatiles analysis was completed using Static Headspace GC/MS. While this method is not certified for fish tissue – it is routinely used for volatiles analysis of blood specimens. Muscle and a skin surface wipe from one fish were evaluated. Approximately 2 g of fish muscle was macerated and placed it in a 10 mL Headspace vial. A kimwipe was used to collect a surface wipe of the same fish, placed in a 10 mL Headspace vial. Both samples were analyzed by Static Headspace GC/MS. The GC/MS method is is validated for Volatile Alcohols, BETX (including Styrene) and C1-C2 Chloro-carbons. Carbon-Disulfide (CS2) has a known retention time, but is not quantitated on this method. Dimethyl Sulfide and Ethyl Mercaptan (aka Ethanethiol) are not characterized, but are expected to chromatograph near CS2.

Chromatograms showed few compounds. There were several aldehydes in both samples -- common aroma compounds. No significant low molecular weight BTEX compounds observed (if BTEX had been positive on surface skin, this could have been a marker for fuel exposure).

Dimethyl Sulfide mass fragments were explicitly targeted in the GC/MS analysis. This focused analysis located a very small peak of carbon disulfide and a C2-sulfide related compound. Mass spectral match indicates either Ethyl Mercaptan or Dimethyl Sulfide, adjacent to Carbon Disulfide. Initial inspection of the chromatogram mass spectrum did not identify the C2-S compound because it is nearly co-eluting with CS2. These compounds were detected in **muscle tissue**- not in surface wipe of the fish skin. Definitive confirmation of these compounds would require authentic reference materials.

While it may be possible the off-flavor aroma originated from CS2/C2-Sulfides in prepared fish, this would not explain any off-aroma compound in this particular whole fish. Also, the aroma of CS2/C2-Sulfides is not consistent with the odors described by the original collectors. Since we don't routinely evaluate fish muscle for flavor compounds, we don't know how common sulfide compounds might be in fish tissue.

Analyst: David Verbrugge
Date of report: 03/05/2019