QuEChERS Extraction Methodology in the Extraction and Determination of PAHs in Shellfish and Finfish from the Gulf Oil Crisis

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Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds included in the European Union and US Environmental Protection Agency (USEPA) priority pollutant list because of their mutagenic and carcinogenic properties. Excluding smokers and occupational vulnerable populations, most individuals are exposed to PAHs predominantly from dietary sources. In the marine environment PAHs are bioavailable to marine species via the food chain, as waterborne compounds, and contaminated sediments. As lipophic compounds that can easily cross lipid membranes and have potential to bioaccumulate in aquatic organisms.

The QuEChERS method has been widely applied in the analysis of pesticides in food since it was introduced by USDA scientists. In general, there are two main steps: extraction and dispersive-SPE cleanup. The first step in the method employs acetonitrile, excess salts and magnesium sulfate (MgSO4) to induce a liquid-liquid partitioning while extracts using very different analytical techniques. QuEChERS method lend themselves nicely to lipophilic compounds that can easily cross lipid membranes, providing relatively clean extracts obtained using the PSA (primary secondary amine) sorbent to remove fats/lipids, and anhydrous MgSO4 to remove any remaining water in the extract.

This application offers a method for the analysis of PAHs at trace levels in fish tissue by GC/MS or GC/MS/MS. The sample preparation approach used here demonstrates substantial time savings when compared with more traditional techniques used in the NDAA method for PAH analysis. The relatively clean extracts obtained using the QuEChERS method lend themselves nicely to either liquid or gas phase analysis. Orthogonal results can readily be obtained from the same extracts using very different analytical techniques. Levels of detection substantially below levels of concern are achieved, with 70-100% average recoveries, and RSDs at 3% or lower on average.

FDA: Established Levels of Concern

Table 1: FDA Levels of Concern established for the Horizon Deepwater oil spill, in parts per million (ppm)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Level of Concern</th>
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<tr>
<td>1 ppm</td>
<td>2 ppm</td>
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<tr>
<td>10 ppm</td>
<td>25 ppm</td>
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<tr>
<td>100 ppm</td>
<td>250 ppm</td>
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QuEChERS Sample Preparation Workflow

1. Weigh 3 g of homogenized fish sample (1 g) in 58 mL centrifuge tube
2. Add surrogate/IS solution, and GC spike solution if necessary vortex 1 min
3. Add 12 mL of DI water and 2 ceramic homogenizers to the sample (Agilent p/n 5982-8P)
4. Vortex 1 min, centrifuge @ 13,000 rpm for 2 min for 2 mL tubes
5. Transfer 500 µL extract to autosampler vial, Agilent p/n 5982-5755 tube
6. SPI SPE 15 mL packet (Agilent p/n 5982-5755)
7. Centrifuge @ 4000 rpm for 5 min
8. Transfer 500 µL extract into autosampler vial, Analyze by GC/MS or GC/MS/MS

Conclusions

• QuEChERS offers a simple sample preparation approach to the extraction and analysis of PAHs in fish and shellfish.
• The simplicity and quickness associated with QuEChERS sample preparation allows multitudes of samples to be processed per day versus per week.
• A pressurized-spike analyzer can help your lab start running PAHs with higher productivity.
• Backflushing will reduce cycle time and instrument maintenance for samples with matrix.
• Signal-to-noise is about the same on a 5975C-QQQ using SIM compared to a 7000B-QQQ using MRM for clean samples.
• The 7000B-SQD can reach lower detection limits for PAHs, with greater confidence than the 5975C-QQQ for QuEChERS extracts for seafood.