

The QuEChERS Approach with GC-TOFMS and GCxGC-TOFMS for PAHs in Oil Contaminated Seafood

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Fresh Seafood QuEChERS Extractions

- Homogenize fresh seafood (scallops, shrimp, oysters) with an equal part of water.
- Put 10g of homogenate in 50mL FEP centrifuge tube.
- Spike with PAHs (100µL under the surface) for recovery studies.
- Vortex for 5 min to disperse spike. Allow to set for 30 min.
- Extract with 10mL acetonitrile using aggressive vortex for 15 min.
- Add EN 15662 QuEChERS salts (Restek# 26236-408).
- Extract for 15 min with aggressive vortex.
- Centrifuge at 3000g for 5 min. Q-sep 300 centrifuge (Restek# 26230).
- Shake 1mL supernatant extract with 150mg MgSO₄ + 50mg PSA + 50mg C18 in FEP tubes.
- Withdraw clean extract and analyze with GC-TOFMS.

Fast GC-TOFMS

- LECO Pegasus 4D GC- and GCxGC-TOFMS.
- 1µL splitless injection at 250 C, purge valve time 30 sec.
- 15m x 0.25mm x 0.25µm Rxi-5Sil MS (Restek# 13620).
- Helium carrier, constant flow, 2 mL/min.
- 90 C (0.5 min), 25 C/min to 350 C (1.1 min), 12 min run time.
- Source temperature 250 C, electron ionization (70 eV).
- Acquisition range 45 to 550u at 20 spectra/sec.
- Quantification against solvent standard.

Q-sep™
QuEChERS Products



Results in ng/g for QuEChERS extractions and fast GC-TOFMS of 10 and 100 ng/g spikes of fresh seafoods. Values in red are biased high due to isobaric interferences.

PAH	Q Mass	Scallops			Shrimp			Oysters		
		100 ng/g	10 ng/g	No spk	100 ng/g	10 ng/g	No spk	100 ng/g	10 ng/g	No spk
Fluorene	166	101	11	1	110	10	ND	103	10	1
Phenanthrene	178	99	9	1	104	9	1	99	9	3
Anthracene	178	99	9	1	105	10	ND	98	10	1
Fluoranthene	202	99	8	2	105	10	ND	108	10	5
Pyrene	202	99	9	1	102	9	1	104	9	4
Benzo(a)anthracene	228	105	9	1	103	10	ND	123	12	2
Chrysene	228	104	10	1	103	11	ND	126	12	3
Benzo(b)fluoranthene	252	103	9	ND	98	9	ND	111	12	ND
Benzo(k)fluoranthene	252	103	11	ND	104	8	ND	122	14	ND
Benzo(a)pyrene	252	102	10	ND	98	8	ND	109	12	ND
Indeno(123cd)pyrene	276	124	37	ND	89	38	ND	117	20	ND
Dibenz(ah)anthracene	278	107	12	ND	105	10	ND	107	13	ND
Benzo(ghi)perylene	276	115	18	ND	99	11	ND	122	31	ND



NIST Standard Reference Material 2974a Organics in Freeze-Dried Mussel Tissue (*Mytilus edulis*)

- Weigh 1g of mussel powder into 50mL FEP centrifuge tube.
- Add 10mL water. Shake to thoroughly wet powder.
- Vortex for 15 min. Allow to stand for 30 min.
- Extract with 10mL acetonitrile using aggressive vortex for 15 min.
- Add 4g MgSO₄ and 1g NaCl (original QuEChERS salts).
- Extract for 15 min with aggressive vortex.
- Centrifuge at 3000g for 5 min. Q-sep 300 centrifuge (Restek# 26230).
- Shake 1mL supernatant extract with 150mg MgSO₄ + 50mg PSA + 50mg C18 in FEP tubes.



➤ Withdraw clean extract and analyze with GCxGC-TOFMS.

➤ This matrix is too complex for fast GC-TOFMS.

GCxGC-TOFMS

- LECO Pegasus 4D GCxGC-TOFMS.
- 1µL splitless injection at 250 C, purge valve time 60 sec.
- 30m x 0.25mm x 0.25µm Rxi-15Sil MS (Restek# 14123), first dim.
 - 1.2m x 0.15mm x 0.15µm Rxi-1ms, second dim.
- Helium carrier, corrected constant flow, 2.2 mL/min.
- 90 C (1 min), 3.75 C/min to 320 C (2.67 min), 65 min run time.
 - Secondary oven offset +5 C
- Modulator temp offset 20 C, modulation time 3 sec.
- Source temperature 250 C, electron ionization (70 eV).
- Acquisition range 45 to 550u at 100 spectra/sec.
- Quantification against 3 point calib curve from solvent standards.
 - Prepared from NIST Standard Reference Material 2260 (Aromatic Hydrocarbons in Toluene).



Results in ng/g for QuEChERS extractions and GCxGC-TOFMS of mussel. The high-biased values (e.g. Phenanthrene, Fluoranthene, Pyrene, Chrysene, etc.) are NOT from isobaric MS interferences, as GCxGC-TOFMS was very efficient and mass spectra for incurred PAHs were of high quality.

PAH spikes directly into the mussel extract showed an average of 120% recovery, indicating that "matrix enhanced response" was only a minor contribution to the elevated values.

Another extraction using the EN 15662 QuEChERS approach produced similar values, but was higher in matrix co-extractives.

PAH	Q Mass	NIST ng/g	GCxGC ng/g
Naphthalene	128	9.68	36
2-Methylnaphthalene	142	8.1	8.8
1-Methylnaphthalene	142	5.8	4.2
Acenaphthylene	152	NA	2.1
Acenaphthene	154	NA	0.1
Fluorene	166	NA	6.0
Phenanthrene	178	74.4	140
Anthracene	178	2.46	3.8
Fluoranthene	202	287	460
Pyrene	202	186	260
Benzo(a)anthracene	228	31.1	52
Chrysene	228	123.6	270
Benzo(b)fluoranthene	252	41.5	74
Benzo(k)fluoranthene	252	18.95	30
Benzo(j)fluoranthene	252	21.4	25
Benzo(e)pyrene	252	58.9	130
Benzo(a)pyrene	252	9.73	16
Perylene	252	6.80	6.4
Indeno(123cd)pyrene	276	14.9	5.0
Dibenz(ah)anthracene	278	NA	18
Benzo(ghi)perylene	276	23.7	29

Mass spectrum from GCxGC-TOFMS for Fluoranthene in a QuEChERS mussel extract.

