What's That Smell? Trace-level Analysis of Odorants in Water Using High-Capacity Sorptive Extraction

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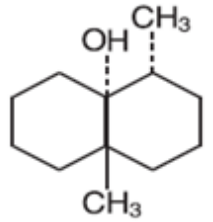
Focus odorants: geosmin and 2-methylisoborneol

- Volatile organic compounds found naturally in water and soils
- A byproduct of bacterial metabolism
- Can impart bad flavor in drinking water and fish grown in ponds or some recirculating aquaculture systems
- Both compounds are lipophilic

Compound Name	Molecular Structure	Formula	Molecular Weight
Geosmin		$C_{12}H_{22}O$	182.3
2-MIB		$C_{11}H_{20}O$	168.3

Diagnostic Research Laboratory at the University of Maine

Aquaculture Research Institute

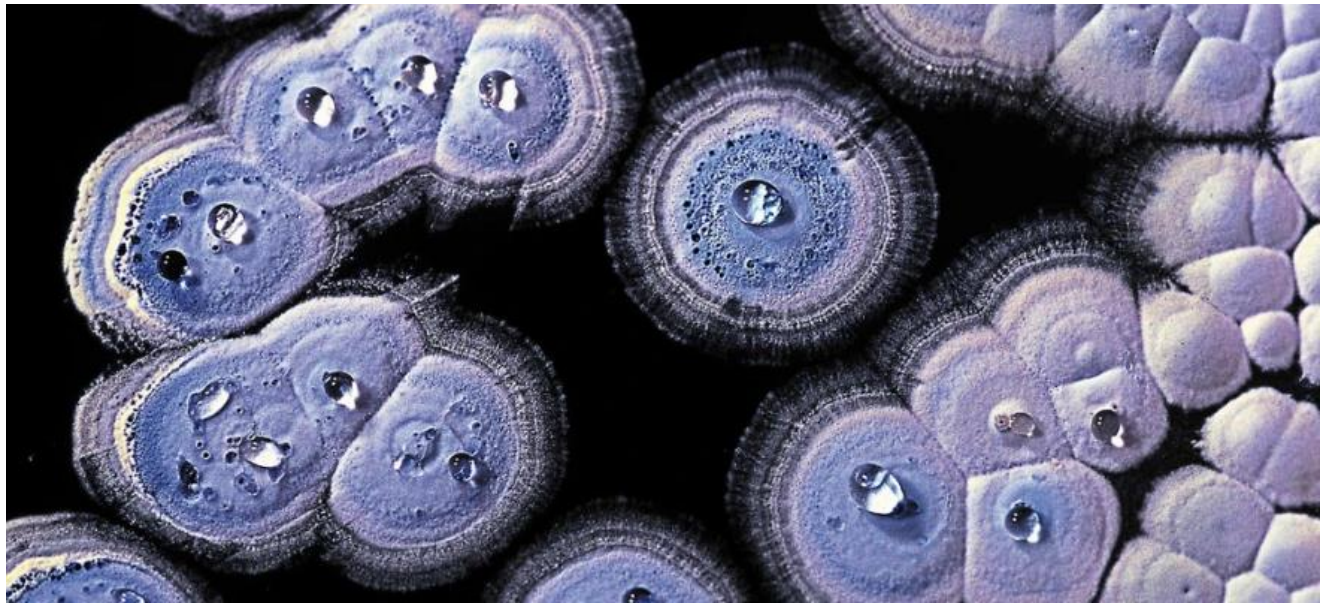
Production of off-flavor compounds in RAS

Geosmin and 2-methylisoborneol (2-MIB) concentrate in fish tissues making them have an earthy flavor

Off-flavor compounds derive from metabolic processes of certain species of:

- Streptomyces
- **Actinomycetales**
- **Myxobacteria**
- **Cyanobacteria**
- Proteobacteria
- fungi

Bolded- commonly found in Aquaculture



Source- https://meristemjourneys.wordpress.com/tag/streptomyces/

Previous methods of detection separation and extraction

- Most previous methods of detection used gas chromatography (GC) for separation with either a mass spectrometer (MS) or flame ionisation detector (FID) for detection
- The major difference amongst methods is how geosmin (GSM) and 2-methylisobrneol (MIB) are extracted
  - Liquid-liquid extraction (LLE)- requires a large volume of sample water
  - Solid-phase microextraction (SPME)- uses a small volume of sorptive phase with low capacity for analytes, which limits extraction efficiency and relies on brittle SPME fibres
  - Stir-bar sorptive extraction (SBSE)- not easily automatable

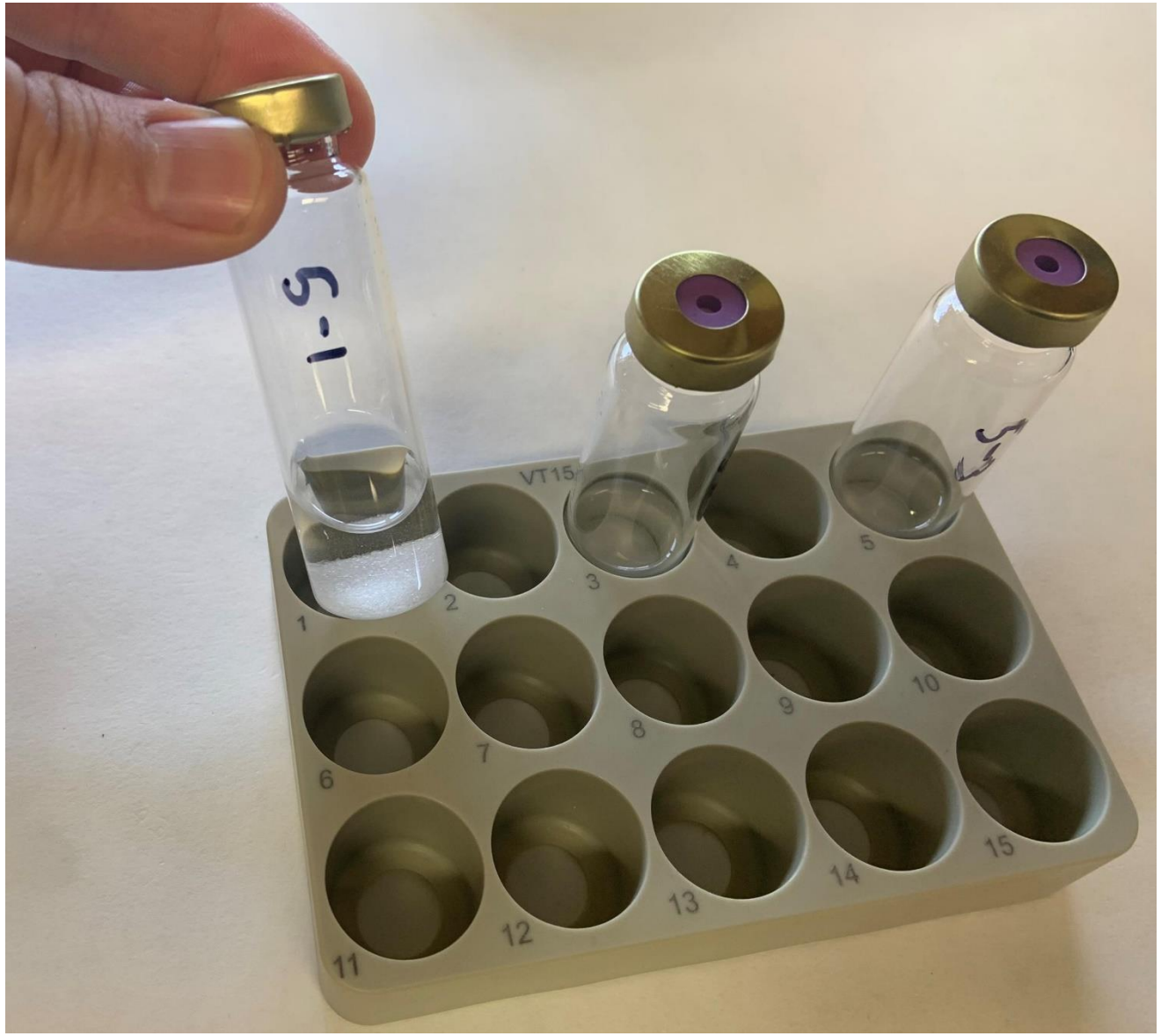
For more on method history see, “An extensive review of the extraction techniques and detection methods for the taste and odour compound geosmin(trans-1, 10-dimethyl-trans-9-decalol) in water” (Bristow et al. 2019)

Our method: sample preparation

5 mL sample water + 2.5 g NaCl added to a 20 mL crimp top vial

2-isopropyl-3-methoxypyrazine (IPMP) then added at 50 ng/L as an internal standard

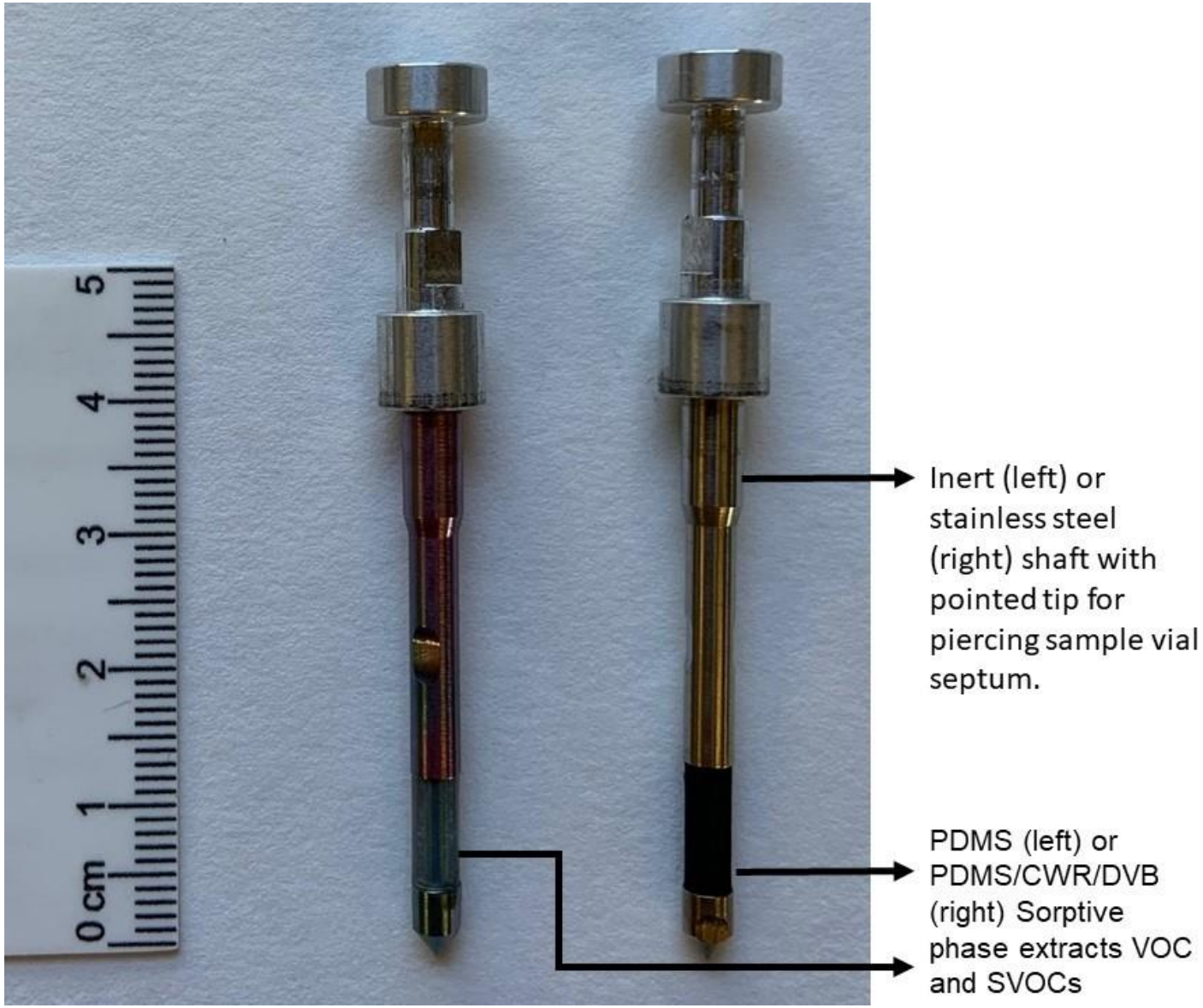
Calibration standards were prepared similarly, except with deionised water containing GSM and MIB at known concentrations between 1 - 200 ng/L



Our method: analytical extraction

Developed an extraction technique using high-capacity sorptive extraction probes and tested two phase types:

- Polydimethylsiloxane (PDMS)
- PDMS with carbon wide range and divinylbenzene (PDMS/CWR/DVB)



Our method: analytical extraction

Pre-incubation phase: Samples heated in the absence of probes for 10 minutes at 65 °C with agitation at 400 rpm to allow analytes to partition from the water to the headspace.

Extraction phase: probes were introduced to the sample vials, and incubation continued for 30 minutes. During this time, analytes partitioned from the headspace to the sorptive phase of the probe.

Probe rinse phase: After removal from the sample vial the probe was rinsed in deionised water to remove residual sample matrix and dried in a stream of ultrapure nitrogen.

Probe desorption phase: The rinsed probe was heated to 270 °C (unless otherwise stated) for 15 minutes in a supply of helium gas, during which analytes were desorbed and transferred to an electrically cooled (25 °C) focusing trap.

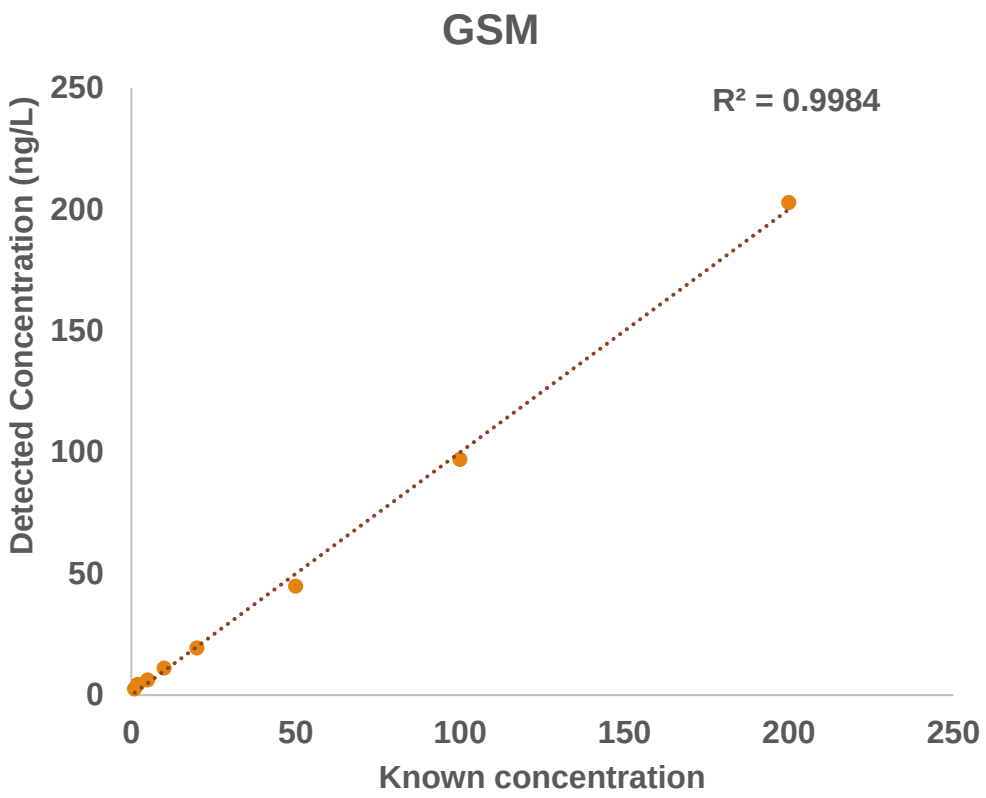
Trap purge phase: The trap was flushed with helium at 50 mL/min for 1 minute to remove residual moisture.

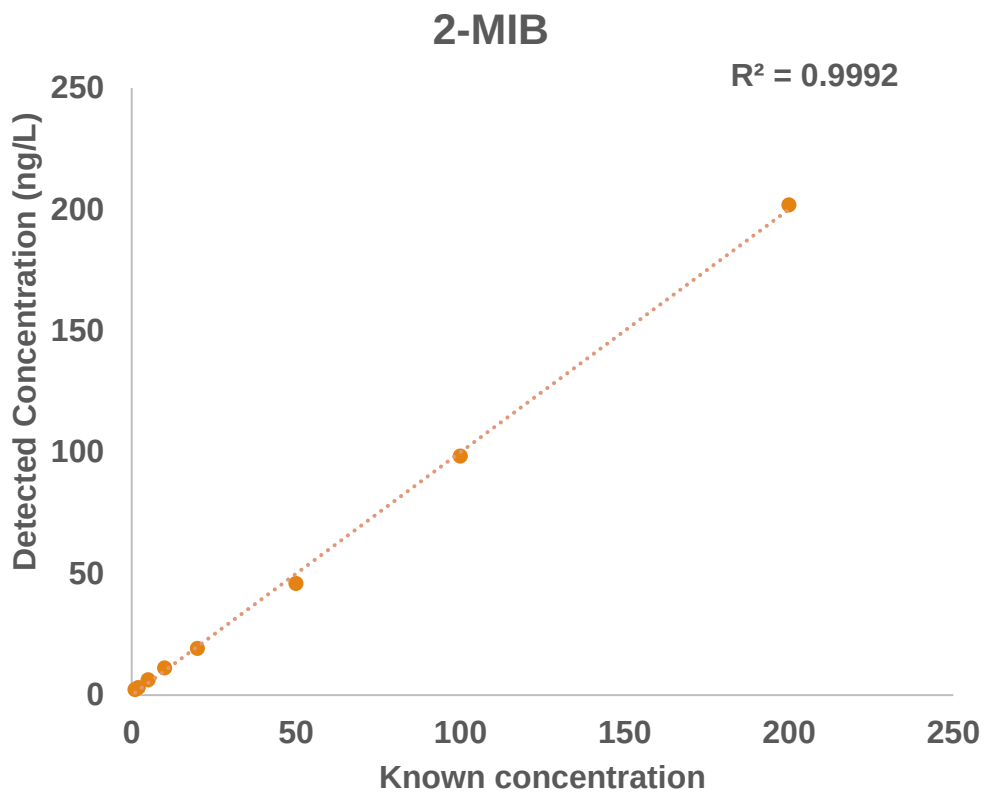
Trap desorption phase: The trap was rapidly heated (>100 °C/sec) to 280 °C in a reverse flow of helium such that analytes were desorbed and transferred to the GC—MS system in a narrow band of vapour. A split ratio of 5:1 was used.

Our method: separation and detection

- GC column- DB-5ms, 30 m x 0.25 mm x 0.25 µm
- Ultra pure helium carrier gas with a carrier flow rate of 2 mL/min
- GC oven program set to 60 °C for 3 minutes then increased in temperature by 10 °C/min to 100 °C, and then by 20 °C/min to 190 °C, and finally by 30 °C/min to 280 °C, holding this temperature for 10 minutes for a total run time of 24.5 minutes
- Transfer line temperature between GC and MS set to 280 °C and temperatures for the ion source and quad were 250 °C and 200 °C, respectively
- MS detection in scan mode, the scan range was m/z 35-350. For selected ion monitoring (SIM) operation, detection was of ions m/z 95 and 107 (for MIB detection), and 137 and 152 (for IPMP) to 10.3 minutes, and of ion m/z 112 and 55 (for GSM) subsequently.

Linearity


GSM
R² = 0.9984
Detected Concentration (ng/L)
250
200
150
100
50
0
0
50
100
150
200
250
Known concentration


2-MIB
R² = 0.9992
Detected Concentration (ng/L)
250
200
150
100
50
0
0
50
100
150
200
250
Known concentration

Carry-over assessment

Analysis	Carryover (%)	
	GSM	MIB
GC Run	0.04	0.08
Trap desorption	0.09	0
Inlet desorption	0	0
Probe redesorption	9.35	3.77

Desorption temperature optimization

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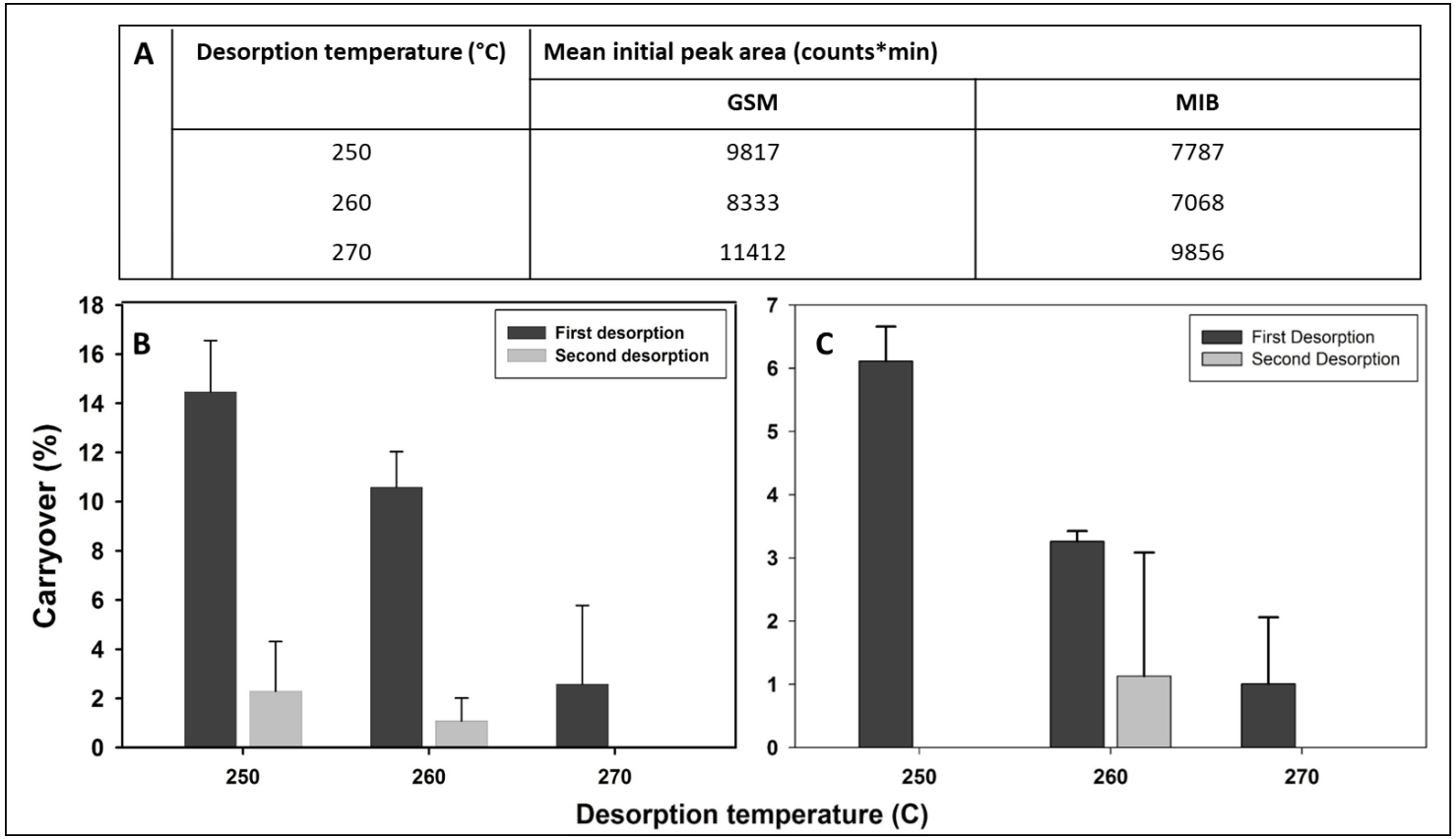
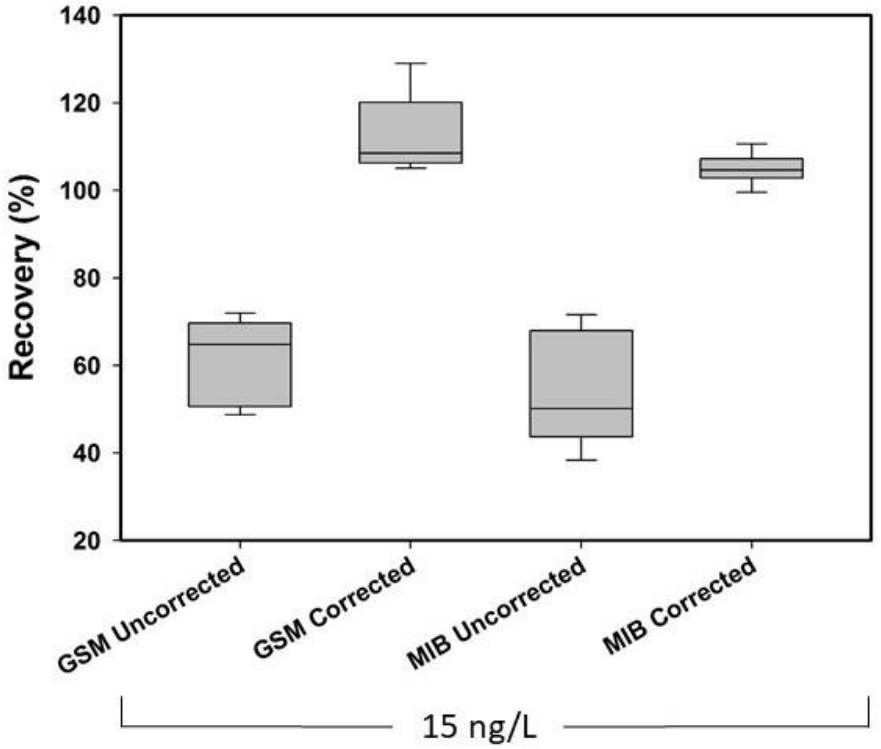
Desorption temperature (°C)	Mean initial peak area (counts*min)	
	GSM	MIB
250	9817	7787
260	8333	7068
270	11412	9856



Internal standard performance



Method detection limit (MDL)

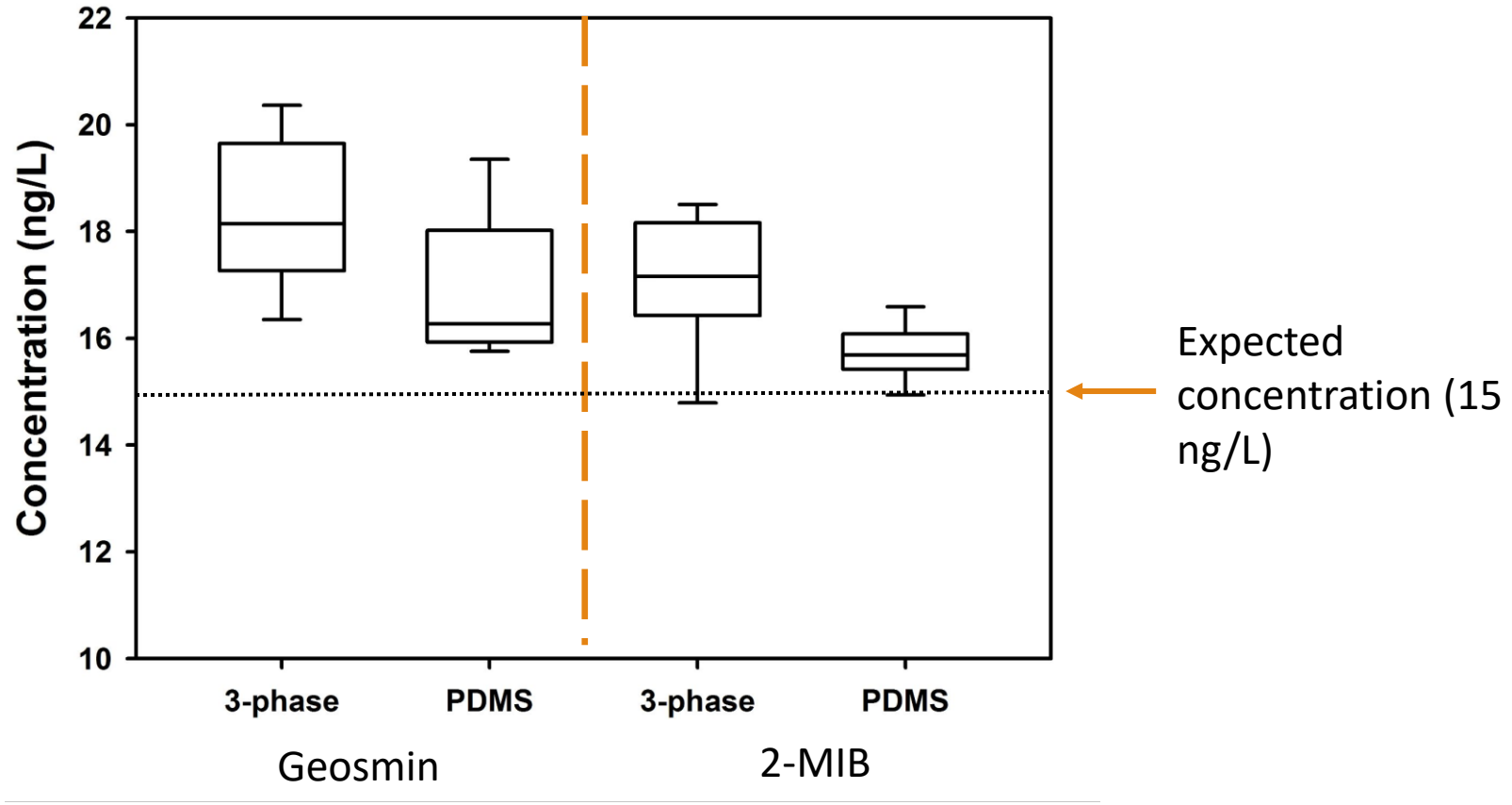
MDL-minimum concentration that can be confidently quantified by the method

We used the procedure outlined by the US Environmental Protection Agency (USEPA 2016) to determine our MDL from 9 samples replicated at 15 ng/L

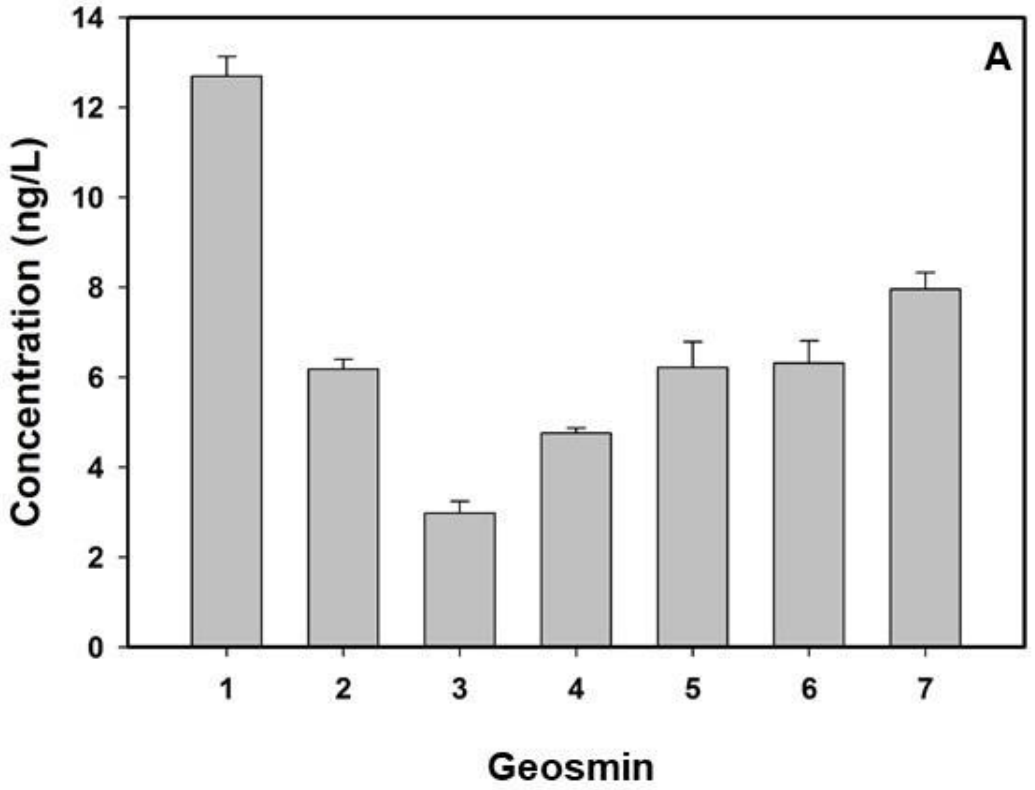
Geosmin MDL: 1.2 ng/L

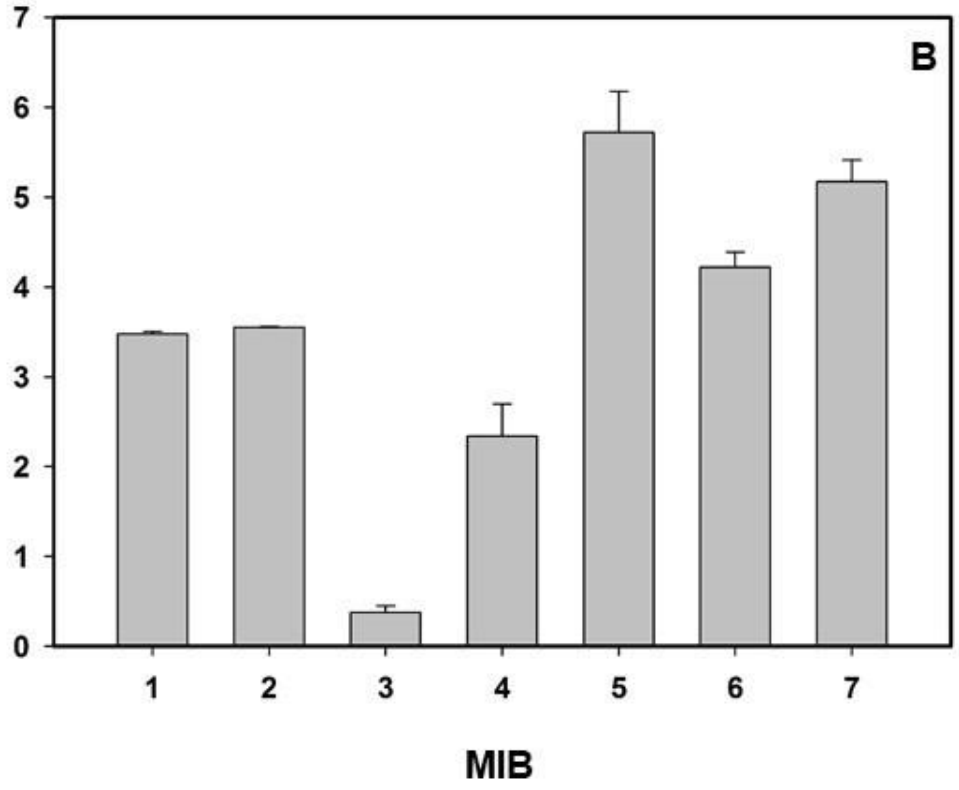
2-MIB MDL: 1.1 ng/L

Sorptive phase extraction



Method applied in aquaculture





Summary

- HiSorb probes are a robust sensitive and fully automatable way to use sorptive phase materials for extraction
- Good linearity on the calibration curve
- Reduced sample preparation time
- Analyze up to 45 samples per day
- Excellent reproducibility with replicates
- Carry-over in method is minimal (1-2%)
- MDLs are below human taste thresholds (10 ng/L)

Our team members