An Optimized Method for the Determination of Haloacetic acids and Dalapon using Quaternary Amine Anion Exchange SPE

EPA Method 552.1

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Overview

- EPA Method 552.1 describes an anion exchange solid-phase extraction followed by methylation and GC-ECD detection for the determination of haloacetic acids and Dalapon in drinking water
- In this study, a silica based quaternary amine cartridge with chloride counter ions was used as the anion exchange sorbent (500 mg).
- Quaternary amine is always charged, so sorbent conditioning with acid and base is unnecessary
- Since the maximum pKa of haloacetic acids and Dalapon is 2.9, a sample pH of higher than 4.9 will charge the analytes

Overview

- Acidifying the sample with sulfuric acid is unnecessary and counterproductive as the sulfate ions will compete with target ions on the sorbent
- With this optimized procedure, less solvent and reagent was used and the total analysis time was reduced by 40 minutes per sample when compared with the original EPA method
- Multiple extractions were carried out simultaneously using a 24-port glass block vacuum manifold

The EPA Method

11.1.2 Conditioning -- Attach adapters and 75 mL reservoirs to the liquid-solid extraction cartridges. To condition the columns, add to the reservoirs and pass the following series of solvents in 10 mL aliquots through the resin under vacuum: **methanol, reagent water**, 1 M HCl/MeOH, reagent water, 1 M NaOH, and reagent water. The conditioning solvents should pass through the resin at the rate of » 2 mL/min. without allowing the resin bed to dry and the sample should be added (Section 11.2.3) immediately after the last reagent water aliquot.

Extraction

1. Add 10 mg ammonium chloride into 100 mL amber bottles to dechlorinate the samples
2. Fill the bottles with 100 mL of water sample. Cap the bottles and shake 1 min. Spike with surrogate and analyte standards accordingly
3. Shake to homogenize the samples
4. Check pH with narrow range pH paper, make sure sample pH>4.9
5. Attach the cartridges to the 24-position manifold. Condition with 10 mL MeOH and 10 mL reagent water at a flow rate of about 2 mL/min. Do not allow the cartridges completely dry out during the condition steps
6. Attach the adaptors and 75 mL reservoirs to the cartridges. Load the samples into the reservoirs
7. apply vacuum to extract the sample at a flow rate of about 2 mL/min
8. Rinse the reservoirs and adaptors with 10 mL reagent water after passing the entire sample through
9. Remove the reservoirs and adaptors, add 10 mL MeOH to dry the cartridges

Extraction

10. Insert 13*100 mm test tubes into the manifold. Attach Clean-Thru tips between the manifold and the SPE cartridges or use positive pressure manifold for elution (H_2SO_4/MeOH solution will corrode nylon bulkhead fittings of the manifold.)

11. Add 2 * 2 mL 10% H_2SO_4/MeOH into the cartridges

12. Elute at 1 mL/ml

13. Turn off the vacuum and remove the test tubes from the manifold

"And I'll thank you to wipe that smirk off your phase!"

Extraction

10. Add 2.5 mL MTBE to the tubes and vortex at low setting for 5 seconds. Place the capped tubes in a heating block, heat at 50 ºC for 1 hour

11. Remove the tubes from the heating block, cool down to room temperature, then transfer to vials (size larger than 20 mL). Add 10 mL 10% Na_2SO_4/water, vortex at high setting for 10 seconds

12. Allow the phases to separate, transfer the upper MTBE layer into a 5 mL vial, repeat the extraction 2 more time with 1 mL MTBE each

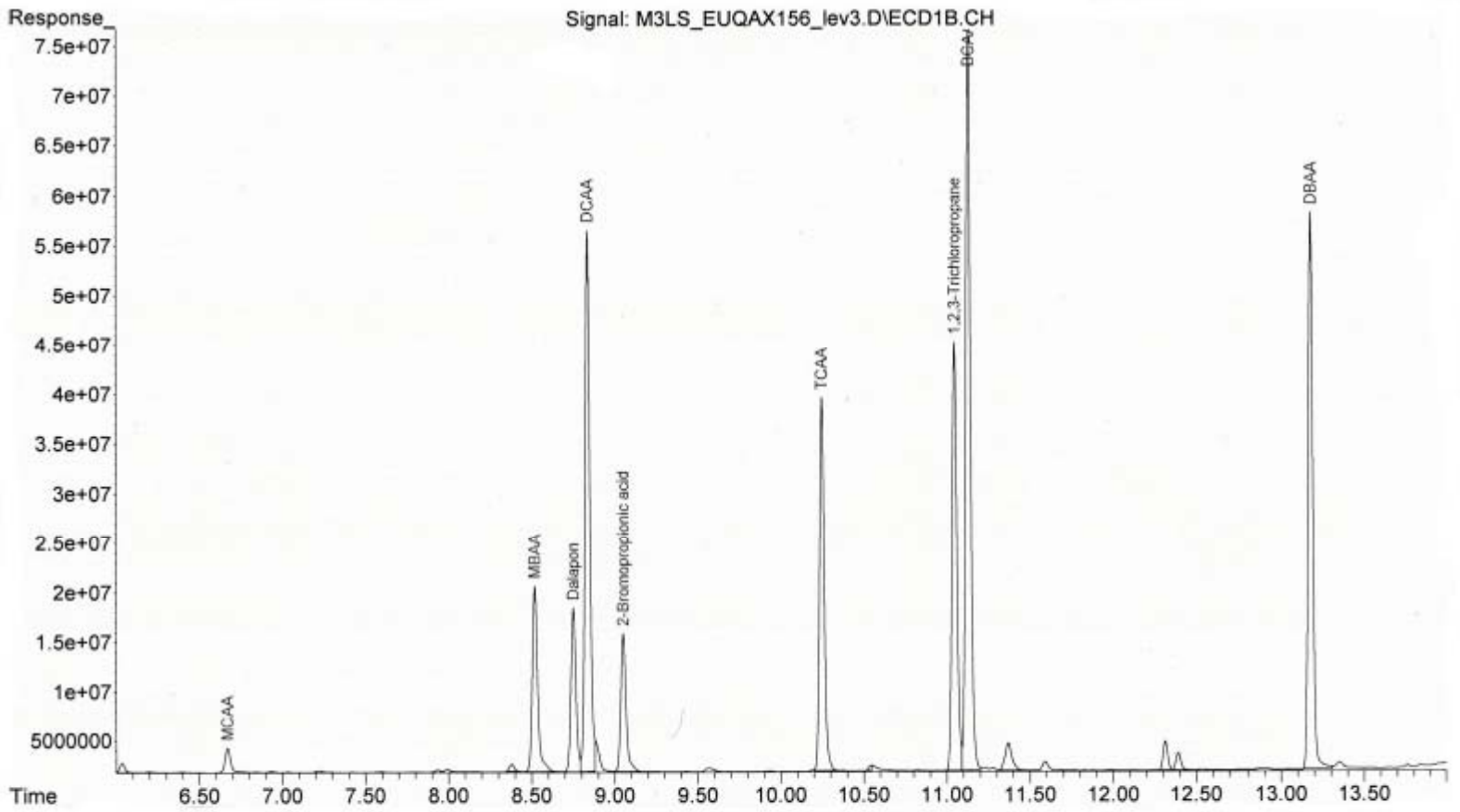
13. Add internal standard, adjust to a final volume of 5 mL with MTBE

14. Transfer 1 mL extract to 2 mL amber vial for GC-ECD analysis.

Analysis

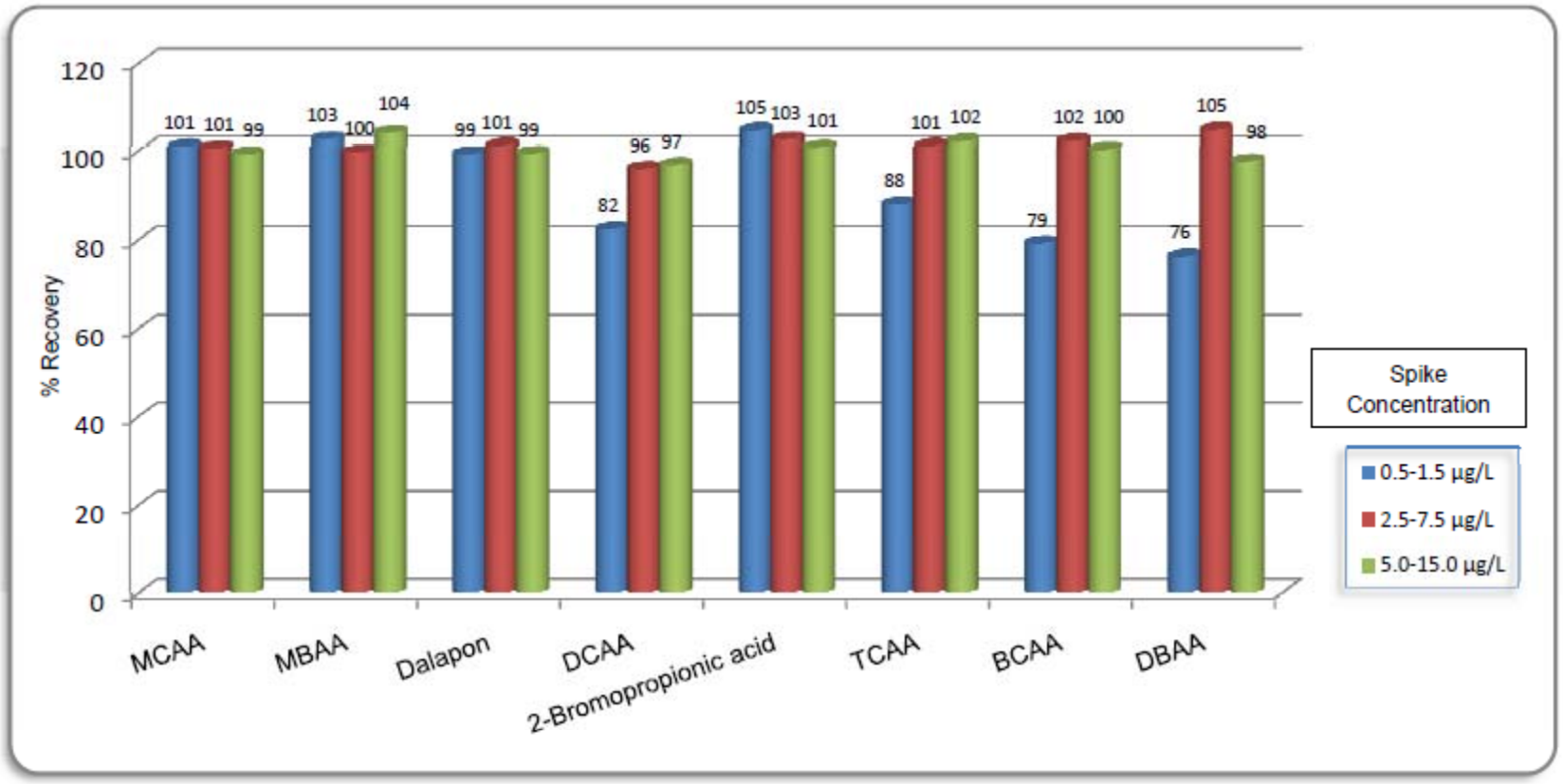
- **GC/ECD:** Agilent 6890N GC coupled with 5975C MSD/ECD, equipped with 7683 auto sampler.
- Chemstation software for data acquisition and analysis.
- **GC capillary column:** Restek Rtx®-1701, 30m*0.25mm*0.25um
- **Injector:** 2 µL splitless injection at 200 ºC, with a split delay of 0.5 min.
- **Liner:** 4 mm splitless gooseneck, 4mmID*6.5mmOD*78.5mm
- **Oven temperature program:** Initial oven temperature of 55 ºC, hold for 5 minute, ramp at 7 ºC/min to 115 ºC, ramp at 40 ºC/min to a final temperature of 280 ºC and hold for 2.3 minutes.
- Total run time is 20 minutes.
- **Carrier gas:** Helium at a constant flow of 1.5 mL/min.
- **ECD temperature:** 280 ºC
- **Make up:** N2 at 30 mL/min
- **Date rate:** 20 Hz, save data from 6 to 14 mins.

Chromatogram Showing Elution of Haloacetic Acids



Analyte Elution Order	RSD @ 0.5-1.5 µg/L %	MDL µg/L @ 0.5-1.5 µg/L	RSD @ 2.5-7.5 µg/L %	RSD @ 5.0-15.0 µg/L %
MCAA	4.6	0.22	1.9	2.2
MBAA	3.2	0.10	1.6	2.0
Dalapon	1.3	0.04	1.0	1.0
DCAA	1.5	0.06	1.1	1.5
2-bromopropionic acid (surrogate)	2.6	0.04	0.6	1.7
TCAA	1.9	0.03	2.2	1.0
1,2,3-trichloropropane (IS)				
BCAA	10	0.25	2.4	3.4
DBAA	10	0.12	2.1	7.6

Analyte Recovery at Various Spike Concentrations (N=7)



Questions?

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