OPTIMIZED EPA METHOD 552.1 FOR THE DETERMINATION OF HALOACETIC ACIDS AND DALAPON IN DRINKING WATER BY QUATERNARY AMINE ANION EXCHANGE METHOD

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INTRODUCTION

EPA Method 552.1 describes an anion exchange solid phase extraction method followed by methylation and GC-ECD detection for the determination of haloacetic acids and dalapon in drinking water. In this study, UCT's silica based quaternary amine cartridge with chloride counter ion (EUQAX156) was used as the anion exchange sorbent. 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. Acidifying 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 total analysis time was reduced by 40 minutes per sample. Multiple extractions were carried out simultaneously using 24-port vacuum manifold.

SPE PROCEDURES

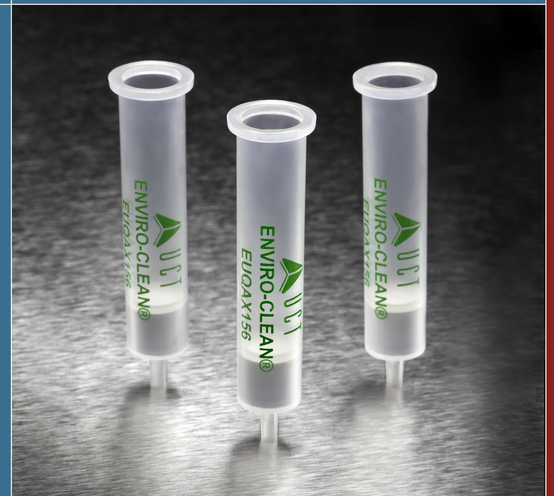
- Weigh 10 mg ammonium chloride into 100 mL amber bottles. Fill the bottles with about 100 mL water sample. Cap the bottles and shake 1 min. Spike with surrogate and analyte standards accordingly, shake to homogenize the samples. Check pH with narrow range pH paper, make sure sample pH>4.9.
- Attach 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 to dry during the condition steps.
- Attach the adaptors and 75 mL reservoirs to the cartridges. Load the samples into the reservoirs, apply vacuum to extract the sample at a flow rate of about 2 mL/min. Rinse the reservoirs and adaptors with 10 mL reagent water after passing the entire sample through. Remove the reservoirs and adaptors, add 10 mL MeOH to dry the cartridges.
- 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 the bulkhead fittings of the manifold.) Add 2 * 2 mL 10% H_2SO_4/MeOH into the cartridges, elute at 1 mL/min. Turn off the vacuum and remove the tubes from the manifold.
- 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 °C for 1 hour.
- 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, allow the phases to separate, transfer the upper MTBE layer (No aqueous phase should be transferred, as it will damage the GC column) into a 5 mL vial, repeat the extraction 2 more times with 1 mL MTBE each. Add internal standard, adjust to a final volume of 5 mL with MTBE. Transfer 1 mL extract to 2 mL amber vial for GC-ECD analysis.

INSTRUMENTAL

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 °C, with a split delay of 0.5 min.
Liner: 4 mm splitless gooseneck, 4mmID*6.5mmOD*78.5mm (UCT: GCLGN4MM)
Oven temperature program: Initial oven temperature of 55 °C, hold for 5 minute, ramp at 7 °C/min to 115 °C, ramp at 40 °C/min to a final temperature of 280 °C 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 °C
Make up: N_2 at 30 mL/min
Date rate: 20 Hz, save data from 6 to 14 mins

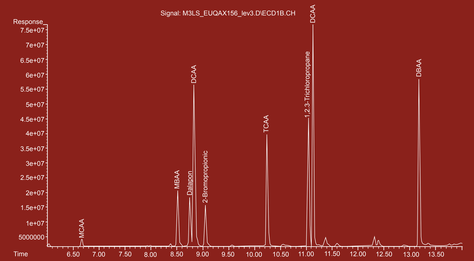
MATERIALS

SPE cartridges: Quaternary Amine with chloride counter ion, 500 mg/6 mL (UCT: EUQAX156)
Adaptor: Tapered fit for 1, 3 and 6 mL **cartridges** to connect reservoirs with a standard luer fitting, ideal for large sample volume (UCT: AD0000AS)
Empty polypropylene reservoirs: 75 mL capacity (UCT: RFV0075P)
Vacuum pump (UCT: ECROCKER400)
24 Position vacuum manifold system (UCT: VMF024GL)
CLEAN-THRU® Tips (UCT: CLTTP050)
Sodium sulfate, anhydrous, ACS, Granular 60 Mesh (UCT: ECSS05K)



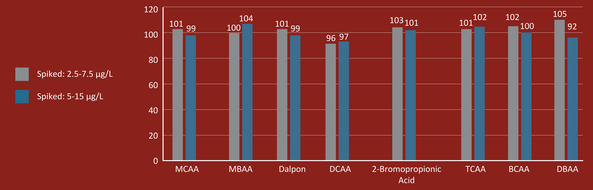
RESULTS

CHROMATOGRAM: REAGENT BLANK FORTIFIED WITH 5-15 µg/L HAAS

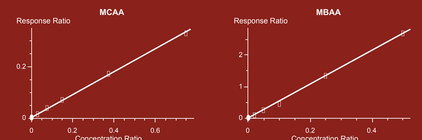


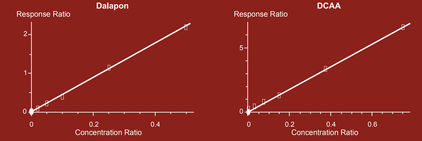
METHOD DETECTION LIMIT AND LINEARITY DATA

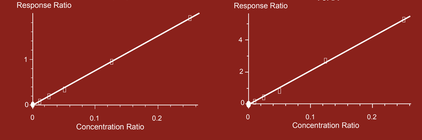
Analytes	Fortified Conc. (µg/L)	Mean Recovery (%)	RSD (n=7) (%)	MDL (µg/L)	LDR (µg/L)	R^2
MCAA	1.5	101	4.6	0.22	0.6-15	0.9993
MBAA	1.0	103	3.2	0.10	0.4-10	0.9994
Dalapon	1.0	99	1.3	0.04	0.4-10	0.9988
DCAA	1.5	82	1.5	0.06	0.6-15	0.9988
2-Bromopropionic Acid	0.5	105	2.6	0.04	0.2-5	0.9995
TCAA	0.5	88	1.9	0.03	0.2-5	0.9981
BCAA	1.0	79	10	0.25	0.4-10	0.9982
DBAA	0.5	76	10	0.12	0.2-5	0.9985

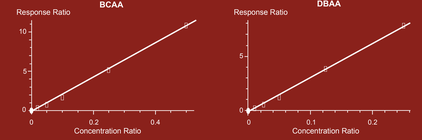


CALIBRATION CURVES









CONCLUSION

With UCT's silica based quaternary amine cartridge (EUQAX156) and modified procedure for EPA method 552.1, excellent recoveries (96-105%) and RSD% (<8%, n=3) were obtained for laboratory fortified samples. Method detection limits between 0.03 and 0.25 µg/L with RSD% (n=7) less than 10% were achieved.