

REMOVING PERCHLORATE FROM THE BRINE OF LAKE VIDA (ANTARCTICA) FOR VOLATILE ORGANIC MATTER ANALYSIS IN A MARS ANALOG.

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Introduction: The presence of perchlorate salts in the Martian soil has significantly hampered our ability to unambiguously detect and characterize organic matter (OM) that is of Martian origin via pyrolysis [1, 2]. The Sample Analysis at Mars (SAM) instrument onboard the Curiosity Rover detected both chlorinated and non-chlorinated inorganic and organic compounds (HCl, O₂, CO₂, dichloromethane, C₂-C₄ chloroalkanes, chlorobenzenes) at Gale Crater [3, 4, 5]. While the source of Cl in these compounds have been ascribed to oxychlorines indigenous to Mars, the source of carbon remains unclear, though a Martian origin is considered likely [5].

Perchlorate salts (0.4-0.6 wt%) in near subsurface soils of polar Mars [6] alludes to the presence of seasonally thin films of liquid water [7]. Recurring slope lineae observed on Mars surface are hypothesized to be the result of perchlorate deliquescence, further supporting the potential presence of contemporary liquid water on Mars [8]. Low eutectic values of hydrated oxychlorine salts may permit the formation of pools of subsurface interstitial waters, especially during warmer periods [9]. Thus, it is important to explore technologies that can aid in the detection of OM in liquid samples that contain ClO₄⁻ on Mars.

Here, we use a perchlorate-specific strong base anion (SBA) exchange resin (Purolite®A530E) to remove ClO₄⁻ from a Mars analog. The sample is a subsurface interstitial brine located in the lower part of the frozen ice of Lake Vida (McMurdo Dry Valleys, Antarctica). Lake Vida brine (LVBr) contains abundant DOC at 48.2 mmol·L⁻¹ [10] and ClO₄⁻ at 49 µg·L⁻¹ [11]. Resin-treated samples were analyzed via solid phase microextraction (SPME) gas chromatography mass spectrometry (GC-MS) [10].

Method: The SBA resin was used as a stationary phase, packed into baked quartz glass columns, to achieve a total resin bed volume (BV) of 1, 3.4, and 10 mL. The packed column was washed with 5 BV of 1M HCl then 20 BV of dH₂O (chromic acid extracted) before flowing through 100 mL of (1) standard 3M NaCl solutions containing 50 µg·L⁻¹ ClO₄⁻ and (2) LVBr.

Results: Previous experiments performed by direct immersion (DI) SPME GC-MS of LVBr shows the presence of volatiles (except for volatile organic sulfur compounds; VOSC's) that are artifacts produced in the GC injector due to the reaction between the byproducts of the thermal decomposition of ClO₄⁻ (O₂, Cl₂) and OM indigenous to the brine [11]. The distribution of

these compounds is dependent on the molar ratio between the ClO₄⁻ and the reduced carbon available in the system.

After flowthrough treatments with the SBA resin, DI SPME GC-MS of standard NaCl solutions were shown to produce trace HCl and abundant DCM compared to none in dH₂O blanks. HCl and DCM is likely formed by the reaction between thermal decomposition byproducts of ClO₄⁻ and OM from the SPME fiber (Carboxen®/polydimethylsiloxane) and/or the resin stationary phase (*N,N*-dibutyl-1-butanamine). This suggests that up to 10 mL of resin is not adequate to remove low levels of ClO₄⁻ from a briny solution, indicating that the binding affinity of the resin to ClO₄⁻ may be influenced by salinity.

DI SPME GC-MS analysis of LVBr treated with 10 mL of resin shows the presence of HCl and DCM, once again indicating the removal of ClO₄⁻ was not complete. The VOSC's were also observed. However, several aldehydes, alcohols, and ketones were detected in the resin-treated LVBr (3-pentanol, 3-buten-2-one, butanal, 3-hexanol, and 2-methyl-2-butanol) that were not observed previously with the untreated LVBr [11], suggesting that resin organic carbon contributed to the pool of OM available for reaction within the GC injector. We are awaiting results on ClO₄⁻ concentration measurements in the resin treated samples.

Conclusions: The methods described here still needs to be refined and further tested. Other perchlorate-specific SBA resins are also currently being tested. We aim to determine resin/LVBr ratio needed to fully remove the ClO₄⁻ from liquid samples in order to facilitate OM analysis. We are also continuing to experiment with batch removal of ClO₄⁻ from LVBr.

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