

GC/MS METHOD DEVELOPMENT FOR SEPARATING LUNAR VOLATILE ICE SIMULANT HEADSPACE GASES

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Various investigators propose the lunar surface contains widely distributed volatiles, especially water-like species, i.e. OH and H₂O [1, 2]. Surface volatiles are theorized to exist as a hydrated regolith layer [3, 4], concentrated in extremely cold polar permanently shadowed regions (PSR) [3], and/or solar wind implantation reservoirs in lunar glasses [5]. The proposed sources of lunar surface volatiles range from cometary impacts, solar wind, or a supply present during moon formation [5, 6].

Future Artemis missions aim to collect and return the samples containing volatiles collected near lunar polar craters or PSRs. We, as advanced curation scientists, are responsible for developing techniques and methodologies for preserving returned sample integrity as much as possible. Pristine volatile-bearing samples are invaluable to the scientific community seeking to unravel the history of the solar system. Realistically, a sample will experience alteration during collection, transportation back to earth, and storage. The Planetary Exploration and Astromaterials Research Lab (PEARL) seeks to understand temperature and pressure effects on high-fidelity volatile-containing regolith simulants, the foundation for the future of cold curation. This abstract outlines

the separation, identification, and quantification of headspace gases over volatile ice feed stock material using gas chromatography/mass spectrometry (GC/MS).

Preliminary objectives concentrated on sample handling, reproducibility, and understanding the elution characteristics for each analyte. Initial GC/MS method development experiments utilized diluted static headspace sample preparation. Diluted samples were used because sampling headspace gases directly from a vial containing liquid analyte resulted in overloading of the column and detector. Overloading is evident based on chromatogram peak shapes and instrument contamination, or carry over, between experiments. A mixture of three alcohols were used for a majority of the sample handling and reproducibility studies. Reproducibility was tested via multiple users, calibration curves, and check standards.

Stock solutions of condensed lunar volatile analytes included methanol, ammonia in methanol, hydrogen sulfide in water, and an equal volume mixture of methanol, ethanol, and isopropanol. Current samples use room air as the headspace sample matrix, however future experiments will incorporate an inert purge gas, such as argon or nitrogen. Three mL

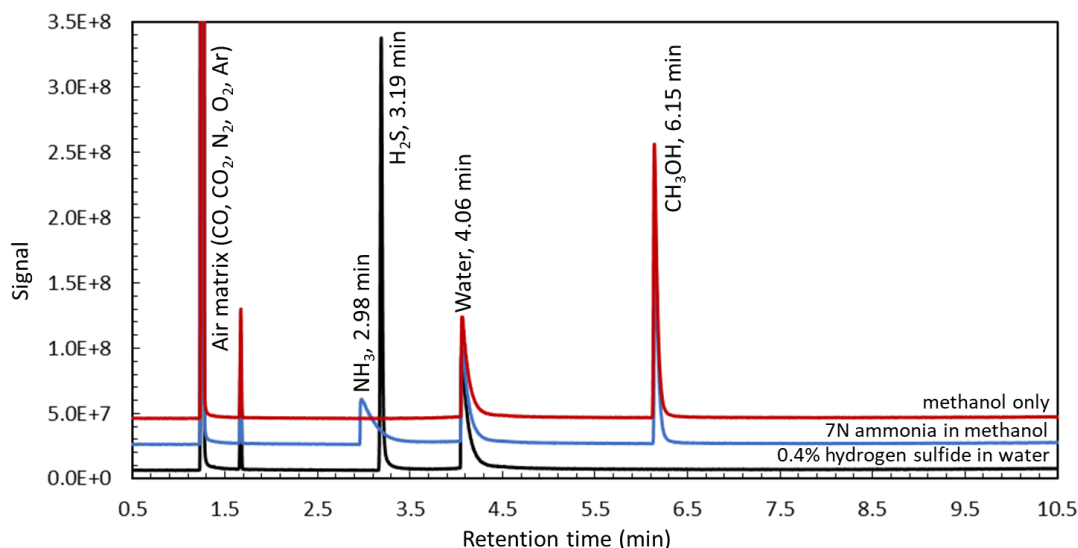


Figure 1. Total ion chromatograms of diluted headspace samples from three lunar volatile simulant solutions: methanol, 7 N ammonia in methanol, and 0.4% hydrogen sulfide in water. Signal has been offset for clarity. Each peak is labeled with the identity (verified via mass spectra) and retention time. Permanent, inseparable air gases elute in the first two peaks, seen above.

of each analyte solution were capped in separate 20 mL crimp top GC vials. Dilutions were carried out by removing an aliquot of headspace gases with a calibrated 1 mL gastight syringe and immediately transferring to a 20 mL capped crimp top vial.

The GC/MS is a Thermo Fisher Trace 1310/ISQ 7000 with a TriPlus RSH autosampler and split/splitless injector module. The experiments outlined in this abstract use the following hardware: a 2.5 mL gastight headspace syringe tool, 1 mm ID x 78.5 mm length ultra-inert straight injection liner, and a TG-BondQ 30 m x 0.32 mm x 10 µm column. Various parameters, such as hardware selection and the temperature, pressure, and split ratio set points, continue to evolve as the overall experiment is refined.

Diluted headspace chromatograms were collected for the individual stock solutions. Retention times, peak shapes, and mass spectra were evaluated and added to the data processing method for each molecule of interest.

Figure 1 shows the total ion chromatograms for the three major lunar volatile simulant stock solutions: methanol, 7 N ammonia in methanol, and 0.4% hydrogen sulfide in water. Tailing peak shapes for ammonia (2.98 min rt) and water (4.06 min rt) indicate the molecules are not properly eluting from the selected column with the current separation method. Additionally, hydrogen sulfide and ammonia have overlapping peak windows, which could impact quantification. Ongoing experiments aim to address the peak shape and overlapping via the separation method and hardware selection.

Sample preparation reproducibility experiments used stock solution containing equal volumes of a non-interactive mixture of methanol, ethanol, and isopropanol. Mass spectrum ion traces were used to identify and quantify all three alcohols. Peaks were automatically detected, identified, and integrated through the mass spectra detection and processing parameters. Calibration response curves and check standards were used to evaluate the validity of the sample preparation procedure.

Figure 2 shows the methanol chromatogram peak area versus total headspace dilution volume transferred from the alcohol mixture vial. The calibration response curves and check standards validate sample preparation procedure.

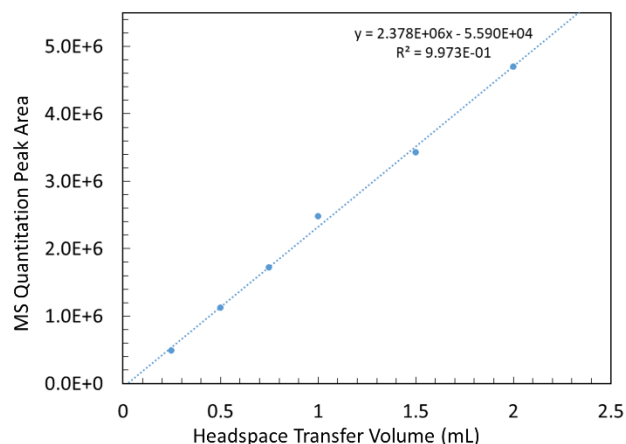


Figure 2. MS Quantitation peak area versus total headspace transfer volume generated a methanol response curve. The stock vial contained a 1:1:1 by volume mixture of methanol, ethanol, and isopropanol at room temperature in air. Similar signal response curves were generated for ethanol and isopropanol as well.

Continuing data analysis efforts are working towards correlating the peak area and instrument response factor to the headspace analyte concentration and condensed phase composition. Static headspace gas chromatography theory relies on Dalton's law, Raoult's law, Henry's Law, and the Kolb and Ettre equation to associate peak area to the analyte composition in a non-ideal solution [7]. Equation 1 is a simplified expression derived from the aforementioned theories.

$$Area = \frac{(RF)C_o}{\frac{p_{total}}{p_i^o} + \beta} \quad (1)$$

Future experiments involve liquid injections of the individual stock solutions, liquid and headspace analysis of various stock solution combinations, and the addition of regolith simulants to the mixtures. Temperature is another variable expected to affect reaction rates and will be explored.

- [1] Colaprete, A., et al. (2010) *Science*, 330, (463-468). [2] Gladstone, G. R., et al. (2010) *Science*, 330, (472-476). [3] Benna, M., et al. (2019) *Nat Geosci*, 12, (333-338). [4] Haruyama, J., et al. (2008) *Science*, 322, (938-9). [5] He, H., et al. (2022) *Research Square*, (1-16). [6] Mandt, K. E., et al. (2022) *Nature Communications*, 13. [7] Snow, N. H. and Bullock, G. P. (2010) *J Chromatogr A*, 1217, (2726-35).