

APPLICATION OF LONG-PATH GAS CELL ASSISTED INFRARED SPECTROSCOPY FOR DETECTION OF LUNAR VOLATILES AND ADVANCED CURATION EFFORTS.

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Introduction: The motivation behind analyzing gaseous samples from the Permanently Shadowed Regions (PSRs) [1] on the lunar surface is built upon the volatiles observed during the LCROSS mission [2]. Advanced curation techniques under cold conditions are essential to the critical scientific analysis of these returned samples [3]. The detection of various volatiles in returned samples by gas-phase infrared (IR) spectroscopy is known to be a powerful tool to understand the resources present in planetary bodies and Astro-materials [4]. The identification and quantification of volatile compounds in returned planetary samples and regolith simulants by advanced and custom-built analytical devices are areas of primary research interest in our group and the Planetary Exploration & Astromaterials Research Laboratory (PEARL) facility.

In this context, we discuss recent advancements and experimental results for quick analysis of the major volatiles detected by the LCROSS (water, CO₂, CH₃OH, and NH₃) by a long-path gas cell/FTIR (Fourier Transform Infrared) spectrometer system [5]. The applicability of this system is demonstrated by qualitative analysis of a series of volatiles measured individually. In addition, the linear dependence of absorption intensity on headspace sample volumes was checked by measuring gas-phase IR absorption spectra of increasing volumes of pure CO₂ gas aliquots. Finally, the instrument performance was evaluated by measuring the relative concentration of NH₃ (g) in methanol solution.

Background: Heteronuclear infrared active gas molecules are qualitatively and quantitatively detectable by the gas-phase infrared spectroscopy. However, measurement of such samples of low concentration in the order of ppm, requires a long optical pathlength cell that incorporates a folded optical path design with extended pathlength within a compact dimension [5]. In PEARL facility, the long-path gas cell (1-16 m variable optical pathlengths, Pike Technologies, Inc.) coupled with a FTIR spectrometer (Nicolet iS50, Thermo-Scientific) allows us to analyze trace components in gas headspace samples. Gaseous aliquots are directly injected to the pre-evacuated long-path gas cell by a gas-

tight syringe (Hamiltoncompany.com) through a custom-built gas injection port and analyzed by a FTIR spectrometer. Our current IR based gas analysis system can acquire a complete absorption spectrum (for a range of 400-4000 cm⁻¹) in under 20 s with optical resolution set at 4 cm⁻¹. In future, advanced version of this system will provide quick upstream analytical data for rapid detection of different IR active lunar volatile compounds.

Sample Analysis Procedure: The IR absorption spectra of a selected set of lunar volatiles were recorded by a long-path gas cell/FTIR spectrometer setup (Fig. 1). The optical pathlength was set at 2.66 meter for all measurements. A known volume of deionized water (10 µL) was directly injected to the pre-evacuated (~40 mTorr) long-path gas cell by a gas-tight syringe and analyzed by a FTIR spectrometer (Fig. 2). A small volume (2 mL) of methanol headspace was extracted from a septum-capped 20 mL stock sample vial containing 3 mL of pure liquid methanol (HPLC grade, purity ~99.9%, Sigma-Aldrich) by a gas-tight syringe and injected to the gas cell/FTIR system and then analyzed. Other headspace samples were analyzed following similar procedure.

Results and Discussions: The effectiveness of this gas analysis system was justified by qualitative analysis of a series of volatiles measured individually.



Figure 1. A glass-bodied long-path gas cell with variable optical pathlength capability, mounted on a Fourier transform infrared (FTIR) spectrometer.

Figure 2 demonstrates a set of gas-phase FTIR absorption spectra for four IR active volatile samples. For NH₃ detection, a (7N) solution in methanol (ThermoFisher Scientific) was utilized. The average acquisition time for each spectrum was less than 20 s. Therefore, our current system is ideal for fast detection of gas species evolving from volatile-containing returned samples.

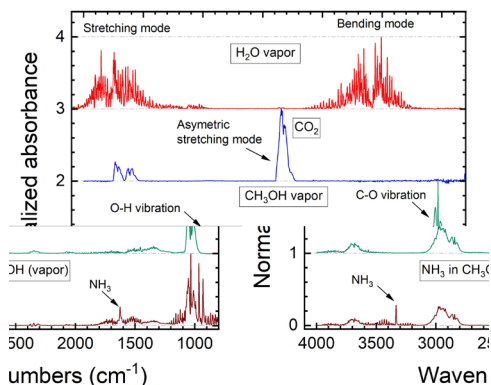


Figure 2. Gas-phase FTIR absorption spectra for a set of four headspace samples. Spectra are normalized and vertically offset for clarity. Main vibrational modes (in some cases) are labeled.

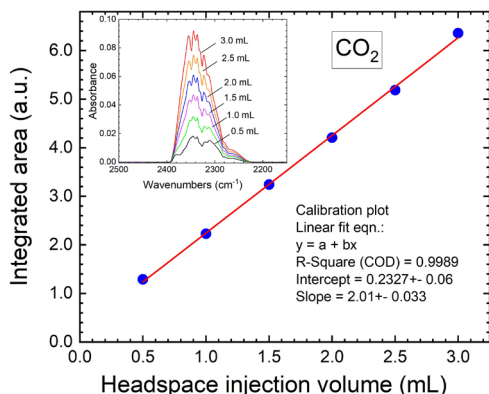


Figure 3. (Inset) FTIR absorption spectra for a set of six samples containing incremental volumes of CO₂ headspaces extracted from a 10 mL vial filled with UHP grade CO₂ at ~1 atm. Integrated area under absorption bands vs. injection volume data are utilized to draw a calibration plot (with a linear fit).

Another glass vial (10 mL) sealed with a crimped cap/septum first purged and then filled with ultra-high purity CO₂ gas at 1 atm. The purity of the gas sample was confirmed by measuring mass spectrum in a UGA 300 instrument (Universal gas analyzer, Stanford Research Systems). Increasing doses (e.g., 0.5 to 3.0 mL) of CO₂ (g) were extracted from the capped stock sample vial by a gas-tight syringe and added to the pre-evacuated long-path gas cell through a customized gas injection port and analyzed separately (Fig. 3). The

linear dependence of integrated absorption areas on gas aliquot volumes further confirms validity of Beer's law for absorption (gas cell fixed internal volume ~ 3.5 L).

To explore the detectability of a single volatile species by our current system in presence of multiple IR active volatiles, a set of increasing volumes of NH₃/methanol headspaces were scanned by the gas cell/FTIR setup. (Fig. 4). Here, increasing doses (e.g., 0.5 to 3.0 mL) of NH₃/CH₃OH vapor were extracted individually from a capped 20 mL stock sample vial containing 1 mL of NH₃ (7N) solution in methanol (ThermoFisher Scientific) by a gas-tight syringe, injected to the pre-evacuated gas cell and then measured by the spectrometer separately (Fig. 4, inset). Like results obtained for CO₂ headspaces (Fig. 3), the integrated area under each NH₃ absorption spectrum (centered at ~3334 cm⁻¹) also varies linearly with the injected sample volumes.

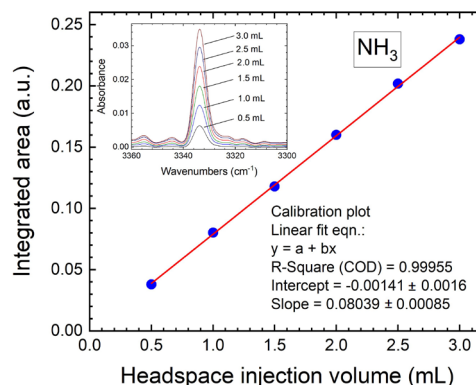


Figure 4. (Inset) A set of six infrared absorption spectra to demonstrate the dependence of the integrated absorbance on the headspace injection volumes of the NH₃/CH₃OH vapor samples. Integrated area under absorption bands vs. headspace injection volumes with a linear fit.

Conclusions and Future Work: We believe that this long-path gas cell/FTIR system is beneficial to both the future study of samples returned from the PSRs and volatile-rich icy regolith simulants for research and curation purposes. Currently, this system is being upgraded for more advanced quantitative analytical detection of volatiles in lunar regolith simulants.

References: [1] Bickel, V. T., et al. (2021) *Nat Commun* 12, 5607. [2] Colaprete, A., et al. (2010) *Science* 330, 463-468. [3] McCubbin, F. M., et al. (2019) *Advanced Curation of Astromaterials for Planetary Science. Space Sci Rev* 215, 48. [4] Lucey, G. P., et al. (2022) *Geochemistry* 82, 125858. [5] Long-Path Gas Cell Installation and User Guide, Pike Technologies, Inc. (2018).