Carbon and Hydrogen Isotope Measurements of Alcohols and Organic Acids by Online Pyroprobe-GC-IRMS Richard A. Socki[1], Qi Fu[2], Paul B. Niles[3], and Everett K. Gibson, Jr[3]. [1]ESCG, [3]KR, NASA Johnson Space Center, Houston, TX 77058, and [2]Lunar and Planetary Institute, USRA, Houston, TX 77058 (richard.a.socki@nasa.gov).

Introduction: The detection of methane in the atmosphere of Mars [1-4], combined with evidence showing widespread water-rock interaction during martian history [5-7], suggests that the production of methane on Mars may be the result of mineral surface-catalyzed CO_2 and or CO reduction during Fisher-Tropsch Type (FTT) reactions [8,9]. A better understanding of these reaction pathways and corresponding C and H isotope fractionations is critical to deciphering the synthesis of organic compounds produced under abiotic hydrothermal conditions. Described here is a technique for the extraction and analysis of both C and H isotopes from alcohols (C_1-C_4) and organic acids (C_1-C_6). This work is meant to provide a "*proof of concept*" for making meaningful isotope measurements on complex mixtures of solid-phase hydrocarbons and other intermediary products produced during high-temperature and high-pressure synthesis on mineral-catalyzed surfaces. These analyses are conducted entirely "on-line" utilizing a CDS model 5000 Pyroprobe connected to a Thermo Trace GC Ultra that is interfaced with a Thermo MAT 253 isotope ratio mass spectrometer operating in continuous flow mode. Also, this technique is designed to carry a split of the GC-separated product to a DSQ II quadrupole mass spectrometer as a means of making semi-quantitative compositional measurements (fig. 1).

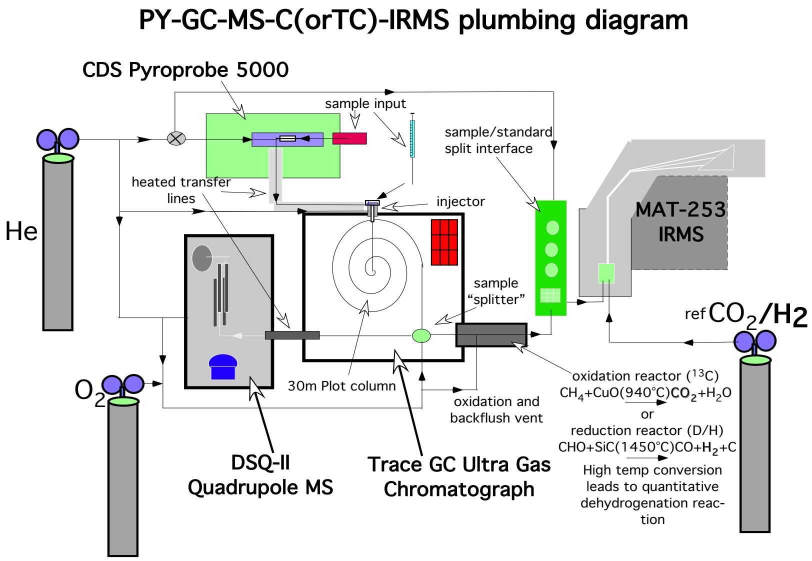

Figure 1. Experimental apparatus showing the pyrolysis, gas chromatograph, quadrupole mass spectrometer, combustion (or high temperature conversion) isotope ratio mass spectrometer.

Therefore, both chemical and isotopic measurements can be carried out on the same sample.

Experiments: Reagent grade alcohols (C_1-C_{4n}) and carboxylic acid (C_1-C_6) were analyzed for their C and H isotope compositions by Pyrolysis-GC-MS-C-IRMS. For H isotopes the combustion furnace is substituted with a high Temperature Conversion (GC-

TC) pyrolysis furnace, following a modified technique described by Burgoyne and Hayes, 1998 [10]. The following experimental conditions were followed: *sample size*: 0.5 to 1.0 ml of alcohol/organic acid injected in pre-baked (850°C) quartz pyroprobe tubes; *GC conditions:* 30 m poraplot Q column, 35°C held for 2 min., ramp to 210°C at 50°C/min., injector held at 180°C, He flow rate = 4.0 ml/min.; *Pyroprobe:* 50°C interface temperature, probe heated to 200-300°C for 30 s., transfer line held at 150°C; *IRMS*: CF mode, 2 ref. injections at beginning of run, He P = 15psi, combustion furnace T = 940°C, GC-TC conversion T = 1450°C.

Results and Discussion: In order to test the reliability of this technique alcohol and organic acid internal standards were analyzed repeatedly for both C and H isotopes. Additionally, traditional sealed tube combustions were performed off-line on the standards and analyzed for their C isotope compositions. Average δ^{13}C valves range from –45.4 (V-PDB) for methanol to –11.4 (V-PDB) for ethanol, reproducibility was typically better than ±1.5‰ for organic acids and ±.8‰ for alcohols. Average δD values range from -247.5‰ (V-SMOW) for ethanol, to -68‰ (V-SMOW) for ethanoic acid. Reproducibility using this method is typically better than ±5.2‰ for organic acids and ±5.7‰ for alcohols. The largest standard deviation between runs is seen in the C-4 organic acid standard and the C-4 alcohols for both δ^{13}C and δD. We postulate that this high standard deviation could be the result of incomplete thermal desorption during pyrolysis (pyroprobe). We are actively investigate the reliability of this technique for making C and H isotope measurements of solids and intermediary mineral surface-catalyzed organic compounds.

Conclusions: Our experiments utilize a pyroprobe interfaced with a GC, quadrupole MS and IRMS to extract and measure C and H isotopes from organic acids and alcohols. These experiments serve as a "*proof of concept*" for making isotope measurements on more complicated mixtures of solid-phase hydrocarbons and intermediary products.

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