

Hydrogen Isotope MicroChemLab FY15

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Abstract

We have developed a new method to measure the composition of gaseous mixtures of any two hydrogen isotopes, as well as an inert gas component. When tritium is one of those hydrogen isotopes, there is usually some helium present, because the tritium decays to form helium at a rate of about 1% every 2 months. The usual way of measuring composition of these mixtures involves mass spectrometry, which involves bulky, energy-intensive, expensive instruments, including vacuum pumps that can quite undesirably disperse tritium. Our approach uses calorimetry of a small quantity of hydrogen-absorbing material to determine gas composition without consuming or dispersing the analytes. Our work was a proof of principle using a rather large and slow benchtop calorimeter. Incorporation of microfabricated calorimeters, such as those that have been developed in Sandia's MicroChemLab program or that are now commercially available, would allow for faster measurements and a smaller instrument footprint.

Results and Impacts

The main output of our work is a journal publication described below. This project began in FY13, and we submitted our manuscript at the end of FY14. In this case, the reviewers asked us to perform more detailed analysis of the sensitivity of our technique. When performing this analysis, we discovered that we had been understating the sensitivity, and undertook further experimental and theoretical work to clarify this. We resubmitted the manuscript in May. Reviewers of this version asked for further detail on sensitivity, including in the presence of tritium (which we addressed theoretically), as well as the applicable pressure range, and ways to extend it. These revisions were submitted at the end of July. The manuscript was accepted in August, and we returned corrected proofs in early September.

Early in the year, we initiated the process to release the software developed to model our experiment as an open-source package through DOE's Energy Science and Technology Software Center. This would make it easier for other researchers to reproduce our results. The software also contains a way to compute the Pd-H phase diagram as a function of isotopic composition, which would be of general value to the hydrogen research community. The software release is intended to be consistent with new Department of Energy plans for sharing and preservation of digital research data, promoted mainly by the Office of Science. The software release process can require a large fraction of a year in order to obtain all of the required reviews and approvals, and we are still waiting for this.

These two outputs consumed most of our project effort this year. Our original plan described two further tasks:

1. Evaluate whether response time will improve if the sensor is scaled down, or becomes fundamentally limited by a chemical process.

We ended up addressing this question in the journal publication. The short answer is that it is not fundamentally limited by a chemical process near the conditions studied. Our work was pushing the

inherent response time of our benchtop calorimeter, and we will require a faster experimental platform with lower heat capacity in order to address that limit. Furthermore, we described ways to improve the rates associated with the chemical processes in the system.

2. Describe possible sensing alternatives that use optical techniques.

In Q1, we performed a literature search on methods to measure gas composition by optical techniques. One concept involved measurement of radioluminescence induced by tritium. Helium and the hydrogen isotopes have some unique spectral properties from the extreme ultraviolet into the visible range. However, the literature suggests that the components are distinguishable only at very low gas pressures. Raman spectrometry is a method that was studied by G. Foltz and C. Melius at Sandia several decades ago using high-power lasers that are bulkier, more energy intensive, and more hazardous than mass spectrometers. Modern advances including diode lasers and microfabricated waveguides could significantly reduce size, power, and hazards, making this technique worth revisiting. This method does not measure helium, but its presence could be deduced through proper calibration and combination with a total pressure measurement.

Conclusions and Future Work

Our work this fiscal year suggests that calorimetry could prove to be a useful complement to mass spectrometry in the compositional analysis of the light gases, and that an optimized calorimeter could be smaller and faster than our benchtop instrument. Optical detection methods are also worthy of further study. Pursuing these further will require investments in new or modified microfabricated components or commercial instruments. Our current work was enabled by an instrument purchase made earlier by another program. Our strategy for the future is to seek opportunities where such an investment is also synergistic with other programs, and can enable advancement of both this and other technologies.

Summary of Findings and Capabilities Related to Aging

No findings relevant to specific component/material aging or capabilities were obtained this year.

Administrative Addendum

- **Related Publications and Presentations:**

David B. Robinson, Weifang Luo, Trevor Y. Cai, and Kenneth D. Stewart. "Metal Hydride Differential Scanning Calorimetry as an Approach to Compositional Determination of Mixtures of Hydrogen Isotopes and Helium." In press, corrected proofs submitted September 2015.

<http://dx.doi.org/10.1016/j.ijhydene.2015.08.033>

David B. Robinson and Trevor Y. Cai, "HDThe calorimetry v.1.0", software submitted to Sandia's Legal Technology Transfer Center.

- **Milestone Status:**

Description	Status
Q1: Perform experiments that address reviewer comments	Complete
Q2: Complete and resubmit manuscript	Complete
Q3: Perform experiments and modeling to address scaling question	Complete
Q4: Final report addressing scaling question and optical sensing	Complete
Overall: Develop sensing approach to the point that it is accepted by a peer-reviewed journal, and address scaling question	Complete

- **Acknowledgement:**

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