

# Quantitative analysis of UH<sub>3</sub> in U metal and UO<sub>2</sub> matrices by neutron vibrational spectroscopy

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**Abstract.** The ignition of UH<sub>3</sub> has resulted in uranium fires. Neutron spectroscopy is proposed to quantify UH<sub>3</sub> in fuel at risk. Spectra of UH<sub>3</sub> in UO<sub>2</sub> and U metal were obtained using two instruments at Argonne National Laboratory and two instruments at the National Institute of Standards and Technology. Analytical standards were prepared with powders of UH<sub>3</sub>, UO<sub>2</sub> and U metal. Linear relationships were found between the mass of UH<sub>3</sub> and the integrated intensity of the inelastic scattering associated with hydrogen motions. We discuss the relative merits of the different spectrometers for this type of measurement.

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Metallic uranium fuel elements stored in humid environments are subject to corrosion from reaction with oxygen and water. Though the mechanism of uranium corrosion depends on several factors, typically it leads to the formation of uranium oxide and uranium hydride. Uranium hydride is a highly pyrophoric material that ignites spontaneously in air at room temperature. Several cases of uranium fires have been documented where it was confirmed that uranium hydride was the source of fuel ignition [1, 2].

The development of a suitable non-destructive technique for identification and quantification of uranium hydride will be highly useful for ensuring the safe handling of fuel elements. Non-destructive methods of analysis utilizing neutrons as a probe are especially appealing since neutrons have very good penetration capability. However, most of the currently existing neutron techniques that measure hydrogen in various materials, are not selective. They determine bulk hydrogen (both bound and unbound) and do not allow for differentiation among different hydrogenous materials, such as water, dissolved hydrogen, metal hydroxides or metal hydrides. As a result, these methods cannot identify the presence of, or estimate the concentration of pyrophoric uranium hydride in the corroded fuel elements.

In this paper Neutron Vibrational Spectroscopy (NVS) was evaluated as a potential technique for the non-destructive analysis of uranium hydride in uranium metal and uranium dioxide matrices. NVS has an advantage over other neutron methods because it provides selectivity through the optical peaks detected in the inelastic neutron scattering spectrum. It is particularly sensitive to materials containing hydrogen since hydrogen has a large neutron incoherent scattering cross-section and large amplitudes of vibration.

## 1 Experimental

To investigate the feasibility of NVS, a set of analytical standards was prepared by mechanically mixing UH<sub>3</sub> with UO<sub>2</sub> or U metal powders. The sample size was on the order of 10 to 20 grams. The concentration of UH<sub>3</sub> in the standards ranged between 0 and 100 wt. %. The enrichment of uranium was 0.2% U-235. A second set of standards was prepared with 50 wt. % UH<sub>3</sub> in a U metal matrix where the overall concentration of U-235 varied from 0.2 to 10 wt. %. This was accomplished by mixing 0.2% enriched UH<sub>3</sub> with 0.2% to 19.4% enriched U metal. The mixtures were assumed to be homogeneous. The powders were sealed inside cylindrical aluminum sample holders (0.95 cm o.d. and 0.64 cm i.d.) filled with a mixture of argon and helium gases.

Neutron scattering spectra were obtained using the Low Resolution Medium Energy Chopper (LRMECS) and Chemical Excitations (CHEX) Spectrometers at the Intense Pulsed Neutron Source, Argonne National Laboratory, and the Filter Analyzer (FANS) and Disk Chopper (DCS) Spectrometers at the National Institute of Standards and Technology research reactor [3–6]. High-energy spectra at LRMECS, CHEX and FANS are observed in neutron energy loss but in neutron energy gain at the DCS. The incident (scattered) neutron energy  $E_i$  ( $E_f$ ) is fixed for LRMECS and DCS (CHEX and FANS).

## 2 Results and discussion

The neutron scattering spectrum for pure UH<sub>3</sub> obtained with the LRMECS spectrometer is shown in Fig. 1. Its structure is

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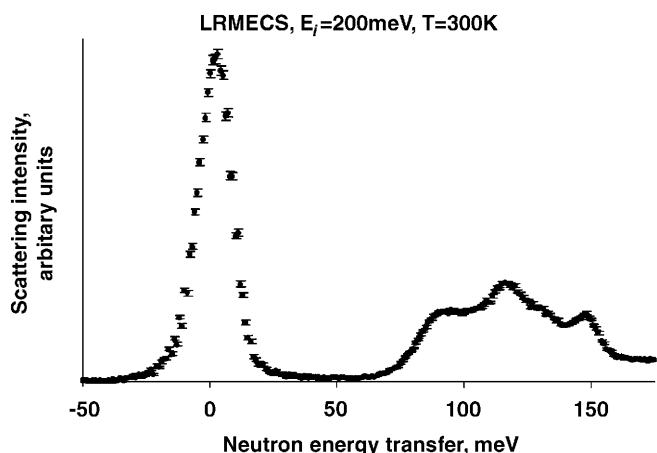


Fig. 1. Neutron scattering spectrum obtained for pure  $\text{UH}_3$  on LRMECS spectrometer ( $E_f = 200$  meV,  $T = 300$  K)

similar to that of spectra obtained with CHEX and FANS. The spectrum consists of a peak centered at 0 meV, corresponding to elastic scattering, low energy lattice modes, plus peaks from  $\sim 80$  to  $\sim 160$  meV associated with hydrogen motions.

Higher order overtones were clearly visible above 160 meV with the CHEX spectrometer.

The fundamental optical peaks of  $\text{UH}_3$  observed using FANS and CHEX are shown in Fig. 2. Corresponding spectra for the  $\text{UO}_2$  and U metal blanks are also shown. Clearly U and  $\text{UO}_2$  do not contribute significantly to the signal in the energy range shown. Areas under the first optical peaks were integrated for each standard and plotted as a function of mass of  $\text{UH}_3$  (Fig. 3). For all four spectrometers a linear relationship exists between the integrated peak intensity of the inelastic incoherent scattering and the amount of  $\text{UH}_3$  in the standards. The limits of detection were estimated at 95% confidence level from the standard error in the estimate of the peak area and the slope of the regression line, and mainly reflect limitations in preparing the standards. The limits of detection and the average sample counting times are summarized in Table 1. Since the individual measurements described in this paper were not necessarily optimized for the determination of  $\text{UH}_3$ , this table should not be used as a means for comparison of the different spectrometers. No attempt was made to measure  $\text{UH}_3$  using standards near the levels of the detection limits.

Table 1. Estimated limits of detection of  $\text{UH}_3$  by neutron vibrational spectroscopy using different neutron spectrometers

Spectrometer	Matrix	Average counting time	Estimated limit of detection, grams of $\text{UH}_3$	Estimated limit of detection, mg of Hydrogen
CHEX	$\text{UO}_2$	2–3 days	1.03	13
LRMECS	$\text{UO}_2$	1 hr	1.25	16
FANS	U metal	1 hr	0.65	8
DCS	U metal	1 hr	1.30	16

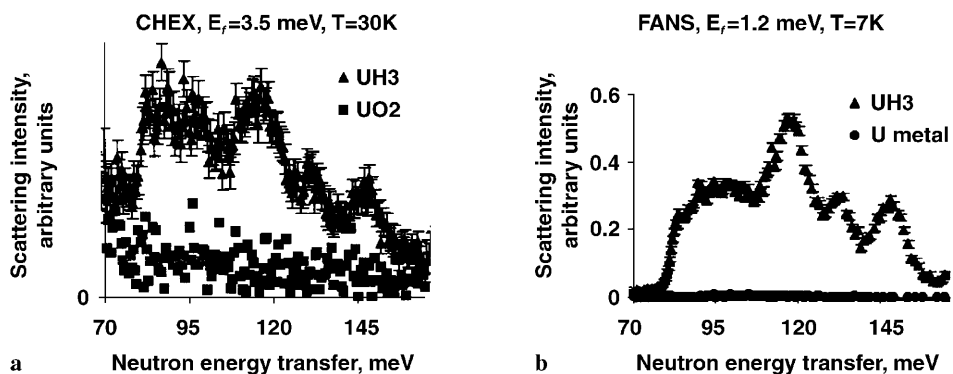


Fig. 2. a  $\text{UH}_3$  optical peaks obtained on CHEX spectrometer ( $E_f = 3.5$  meV,  $T = 30$  K). b  $\text{UH}_3$  optical peaks obtained on FANS spectrometer ( $E_f = 1.2$  meV,  $T = 7$  K)

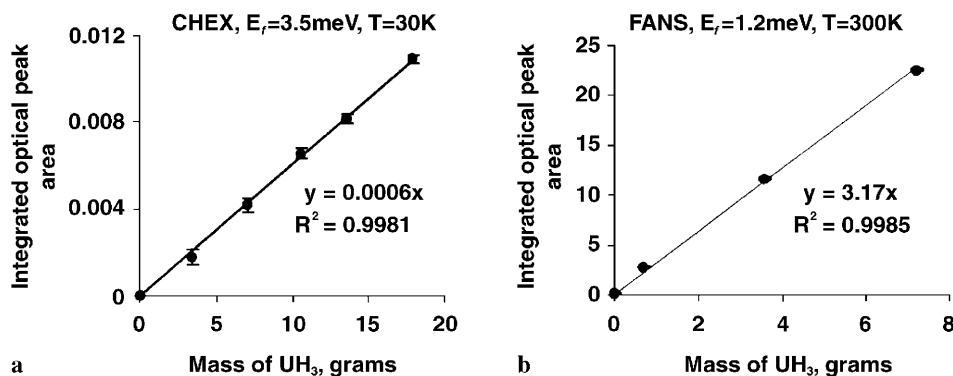


Fig. 3. a Calibration curve for  $\text{UH}_3$  in  $\text{UO}_2$  matrix obtained on CHEX spectrometer ( $E_f = 3.5$  meV,  $T = 30$  K). b Calibration curve for  $\text{UH}_3$  in U metal matrix obtained on FANS spectrometer ( $E_f = 1.2$  meV,  $T = 300$  K)

The time of flight spectrum of  $\text{UH}_3$  obtained on the DCS spectrometer is shown in Fig. 4. The incident neutron energy was 3.5 meV. Four distinct regions are observed: 1) the 0–300  $\mu\text{s}$  range due to U-235 fission neutrons; 2) the peak at  $\sim 900 \mu\text{s}$  due to hydrogen atom motions; 3) the region from  $\sim 1200$  to  $\sim 4700 \mu\text{s}$  due largely to lattice modes; and 4) the peak centered at  $\sim 4860 \mu\text{s}$  due to elastic scattering.

On the FANS spectrometer the background originated from a combination of fast neutrons from the reactor and fission neutrons from U-235 in the sample. This background can be separately measured and subtracted using a cadmium filter positioned behind the sample. At LRMECS and DCS the fast and fission background can in principle be removed by time gating. The increase of background level due to fission with increase of U-235 enrichment for the CHEX instrument is shown in Fig. 5. Clearly elevated background levels at high

levels of enrichment will limit the ability to measure  $\text{UH}_3$  using CHEX.

Spectrometers that utilize incident neutrons of very low energies are more affected by the fission neutron background, since fission is more probable at lower neutron energies. In addition, low energy neutrons are less penetrating. These factors can be important in the selection of a spectrometer for the analysis of corroded fuel elements containing high levels of U-235. The choice of a high energy downscattering time of flight chopper instrument may be preferable for highly enriched fuels due to the decreased U-235 fission cross-section at higher energies and the ability of these instruments to differentiate fission neutrons by time gating.

### 3 Conclusions

These experiments demonstrate that Neutron Vibrational Spectroscopy has potential to become a useful analytical tool for measuring the amount of  $\text{UH}_3$  in U metal and  $\text{UO}_2$  matrices. Though the limits of detection obtained using each of the four instruments are relatively comparable, such parameters as the enrichment of the fuel, signal to background ratio in the region of  $\text{UH}_3$  optical peaks, the length of measurement time and the degree of necessary resolution will determine the optimal spectrometer for the measurement of  $\text{UH}_3$ . It appears that high resolution, high intensity time of flight chopper spectrometers are the preferred choice for this type of measurement.

NVS has promise to fill an important void in the qualitative and quantitative analysis of the chemical species responsible for uranium corrosion.

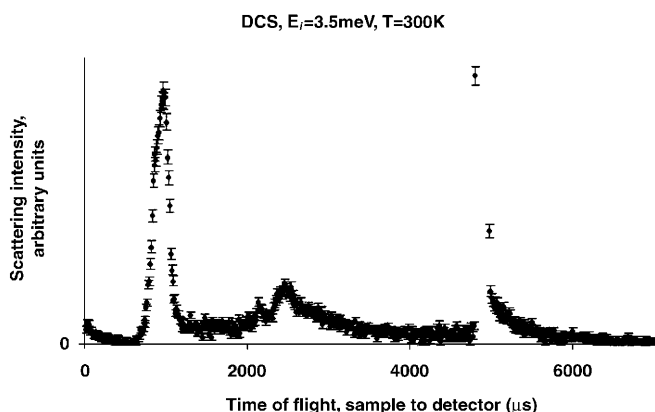


Fig. 4. Time of flight spectrum of pure  $\text{UH}_3$  obtained on DCS spectrometer ( $E_i = 3.5 \text{ meV}$ ,  $T = 300 \text{ K}$ )

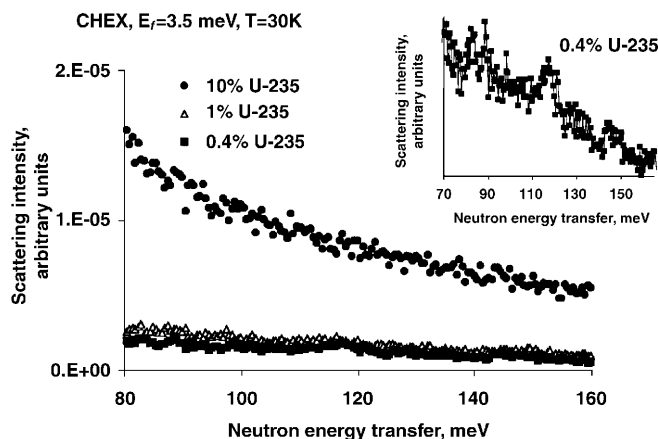


Fig. 5. The effect of U-235 enrichment on the background level near the  $\text{UH}_3$  optical peak area. An *insert* shows the expanded  $\text{UH}_3$  optical peak at 0.4% U-235 enrichment

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