Modified MTS MRB500 Catalyst Performance Test

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ABSTRACT

An experiment was conducted to determine if the oxygen supply in a CuO catalyst considered for use in the TMIST-2 irradiation test would be sufficient to convert all the hydrogen isotopes coming from the irradiation test to water. A mixture of 2% H2 in Ar was supplied to a modified MRB 500 stack monitor from Mound Techology Solutions, Miamisburg, OH. It was found that the catalyst could convert 3.75E-03 moles of H_2 before losing its effectiveness. Conversion was found to begin at a catalyst temperature of about 220°C and to be fully effective at about 300°C.

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BACKGROUND

The TMIST-2 experiment at the Idaho National Laboratory will be seeking to capture very small quantities of tritium emerging from an experiment in an inert gas stream. Because of the small quantities involved, the most reliable means of measurement is scintillation counting of tritium collected in bubbler vials. A standard means of making similar measurements for tritium accountancy in ventilating air stacks is by means of a discriminating bubbler array. One of these is manufactured by Mound Technical Solutions of Miamisburg, Ohio. The standard configuration of their MRB 500 is shown in Figure 1.
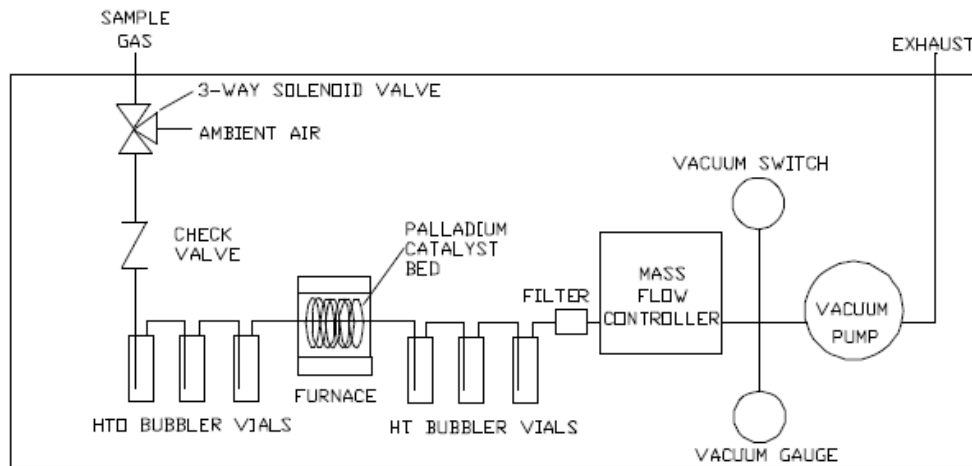

Figure 1. Elements of the MTS MRB 500 in its standard configuration.

These instruments pass the gas stream to be analyzed through a set of 3 bubbler vials in which water soluble forms of tritium are captured. The gas then goes through a Pd sponge catalyst bed where elemental hydrogen isotopes are oxidized. The gas is then passed to the second bank of bubblers where the newly soluble tritium is captured. This allows differentiation as to tritium form in the gas stream.

For the TMIST-2 experiment, a mixture of He and Ne carrying small amounts of tritium will be pushed through the system from pressurized gas bottles. There is no need for the vacuum pump, the mass flow controller and related equipment. With the entire system at atmospheric pressure or above, the ambient air inlet valve would not be functional, so it too may be omitted.

In the conventional application, the carrier gas is air in which there is typically 19% oxygen for oxidizing the tritium in the catalyst bed. For the TMIST-2 application, the carrier gas will be a mixture of He and Ne with no oxygen. Therefore, it was decided that the Pd sponge catalyst bed could be replace with CuO, which could furnish the oxygen for the oxidizing reaction, at least for a time. That leaves the instrument configuration as shown in Figure 2.
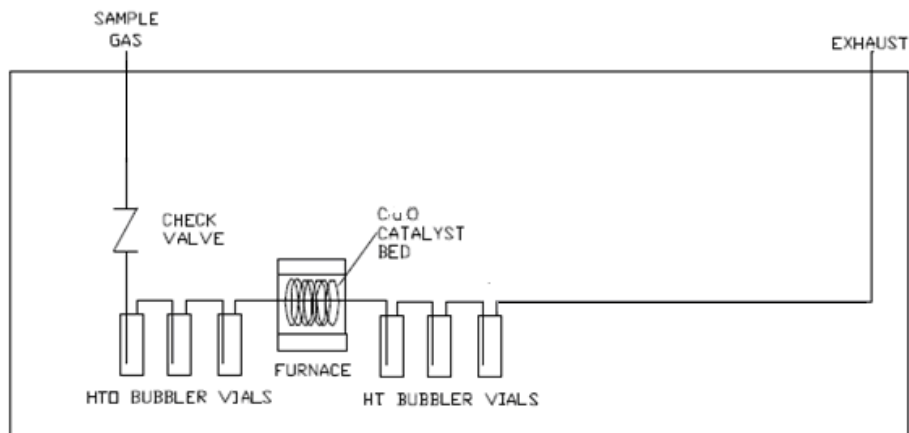
Figure 2. Configuration of modified MRB 500 stack monitor.

There are two concerns with this selection of means for capturing the tritium. One is whether or not the CuO catalyst can supply enough oxygen to perform its intended function over the life of the experiment. The second is whether the small quantity of tritium involved will get lost in the catalyst housing and other structures or come through for an accurate measure of the tritium in the gas stream. The second concern is not admissible of testing without actually using tritium in the small quantities anticipated for the TMIST-2 application. Further, these instruments have been used for many years and have not demonstrated the propensity for holdup of the tritium in the catalyst bed. The presence of the water from the first bubbler array no doubt contributes to minimizing or eliminating any such hold up. Therefore, there is every reason to believe that hold up will be at most a transient delay in the measurement of the tritium coming from the experiment to the bubblers. The other concern, oxygen sufficiency, is the reason for the present experiment.

EXPERIMENT

To determine the extent of oxygen availability of this CuO catalyst, hydrogen bearing argon was flowed over the catalyst bed at a known rate, passing through a mass spectrometer. By observing the time at which the catalytic reaction stopped, we get a measure of the oxidizing capacity of the specific configuration of this instrument.

Apparatus

The configuration of the experiment is shown in Figure 3. The Ar supply was a size K bottle of research grade Ar. After trying several different bottles of D_2 – Ar mixtures, none of which had signals sufficiently visible on the mass spectrometer because of the low D_2 concentrations, we ultimately used a small bottle of Ar – 2% H_2 as the hydrogen supply.
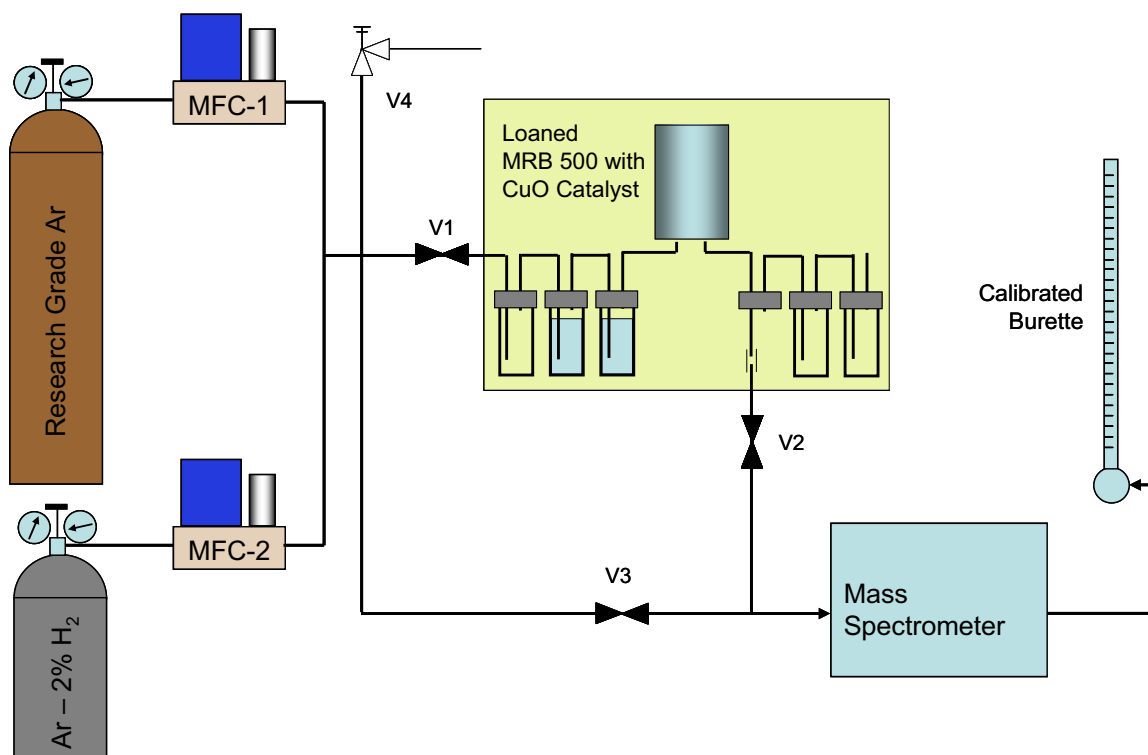
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Figure 3. Experiment configuration for evaluating catalyst performance.

Mass flow controllers (MFCs) were Teledyne Hastings HFC-304 units that had been calibrated for N_2 at 30 psig inlet pressure. One was supposed to be full scale at 5 sccm but actually gave about 10.5 sccm. The other was supposed to be 20 sccm at full scale but actually gave almost 60 sccm. The MFCs were controlled using a Teledyne Hastings THPS 400 four-channel control unit. We were working with Ar at about 20 psig inlet pressure because the available pressure relief valve, V4, required for safety, opened at about 26 psig. Because we had no confidence in the flow calibration of the MFCs, we used a calibrated burette in which a soap film meniscus travels upward through a calibrated volume in measured times to determine flow rates very accurately. This was used to find the flow rate commanded to the supposed 20-sccm MFC that gave the same 10.5-sccm gas flow measured through the supposed 5-sccm MFC.

The mass spectrometer consisted of a SRD CIS 200 quadropole evacuated by a BOC Edwards EXT 70H 24V turbomolecular pump backed by a BOC Edwards XDS 5 scroll pump. Sampling was done through a Varian M1515106 leak valve adjusted to provide gas pressure in the quadropole of about 5E-06 torr. The incoming gas flow passed through a 1/8-inch tube directly against the leak valve inlet port. Control and data display were provided by SRS RGA Version Release 3.004 software on a Dell Optiplex GX110 PC. It was operated in RGA mode at 70 V ionizing potential at 50 µA emission current and 90 V focusing voltage. Even though the quadropole housing had been baked under vacuum and operated with no gas flow for several days, the signal was very noisy. It was difficult but possible to distinguish the mass-2 peak from noise at the 2% concentration.

The valve configuration shown in Figure 3 allowed us to run gas with or without the H_2 component either through the MRB 500 or around it. Most of the tubing in the system was 316

SS, but some lines were ¼-inch PVC. We experimented with line type, replacing PVC with SS in an attempt to reduce system noise, but we saw no significant difference. Connections were mostly Swagelok compression fittings with some VCR and some NPT with Teflon tape on gas bottle regulators.

Experiments

After two days of working with the system and finally arriving at a combination of gas composition and settings that seemed to work, the first test was to demonstrate that the mass-2 signal was clearly present and visible. This was done by alternately flowing gas with and without the H_2 present at the 10.5-sccm flow rate through the bypass line, going around the MRB 500. Some results are shown in Figure 4.
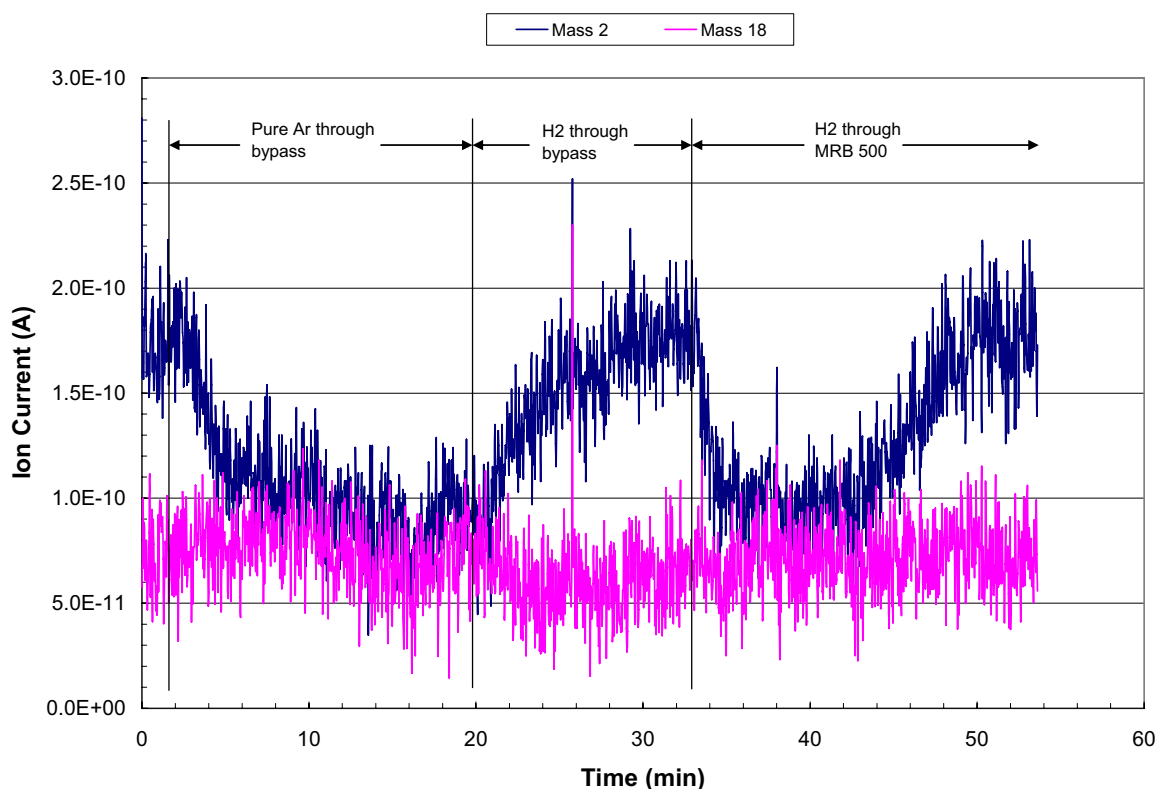

Figure 4. Test data for initial mass-2 visibility determination.

These data begin with H_2 flowing through the bypass. The ion current was about 1.8E-10 A. At approximately 2 minutes into the scan, the gas flow was changed to include only Ar at nearly the same flow rate. There was a short lag while the changing gas composition reached the mass spectrometer. Then, the ion current fell in a time commensurate with some mixing taking place in the gas lines and some H_2 trickling in from dead spaces in the gas lines not on the direct flow path. After about 15 minutes, the signal had reached the system background level.

At 20 minutes into the scan, the H_2 was readmitted to the gas stream. The reverse process took place in the mass-2 signal. The apparent variations in the mass-18 signal during this time were correlated generally oscillations in pressure in the quadropole. They suggest that the mass flows

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through the 2 MFCs were not quite balanced. Only one was open at a time, MFC-1 when only pure Ar was wanted and MFC-2 when the Ar – 2% H_2 was flowed. Subsequent measurements through the calibrated burette showed the flow through MFC-1 was 8.46 sccm while that through MFC-2 was 7.06 sccm.

At 33 minutes into the scan, the gas with H_2 was redirected through the MRB 500. The mass-2 signal immediately fell but then recovered as the volume of the catalyst bed and the gas lines in that part of the experiment became filled with the H_2 mixture. It is noteworthy that there was no observed increase of mass 18 during that time. The gas coming out of the second bubbler should have been saturated with water vapor at 20.8°C (2.8% of the local atmospheric pressure), a little greater fraction than the H_2. Even if there was a delay while tube wall surfaces became saturated with adsorbed water, it should have risen eventually. We did not see any evidence of the mass 18 signal changing in the experiment.

With H_2 bearing gas flowing through the MRB 500, we then started on a temperature ramp to evaluate the temperature at which the CuO became effective in catalyzing the oxidation of the H_2. These results are shown in Figure 5.
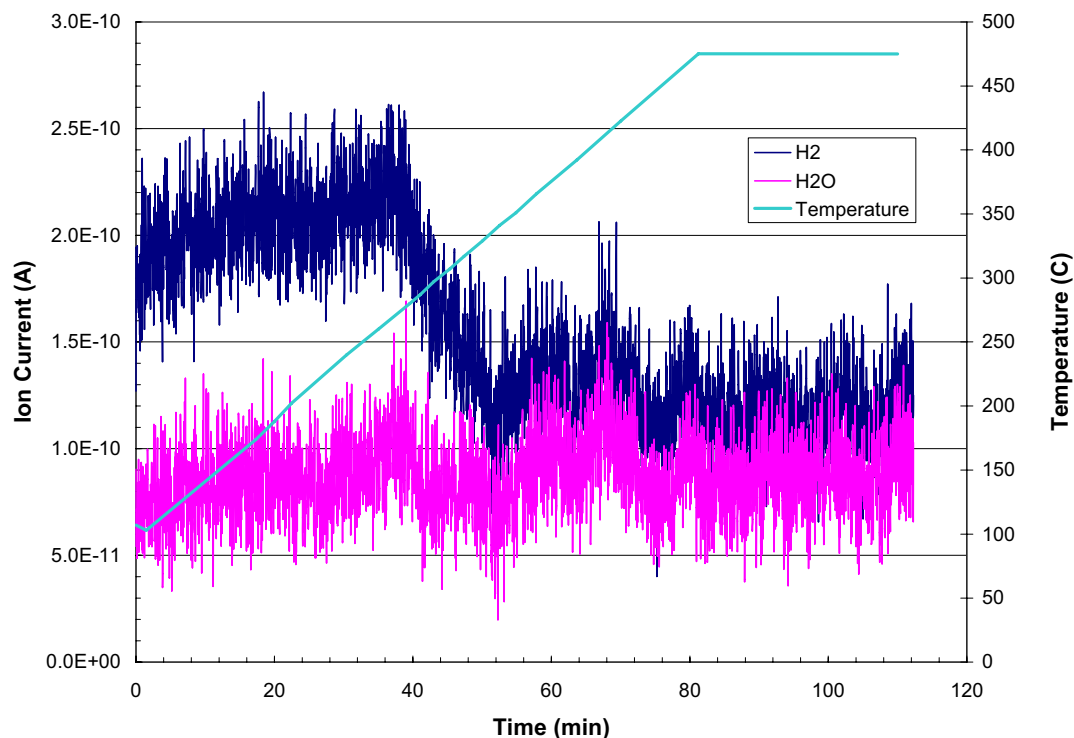

Figure 5. Catalyst performance with temperature.

The temperature ramp started at about 103°C (we had kept the catalyst at just over 100°C to try to keep it dry). Over the course of 80 minutes, the temperature increased linearly to 475°C. Considering the time lag for transport from the catalyst to the mass spectrometer, it appears the catalysis began at about 220°C, consistent with results from other experiments performed for this project using CuO catalyst.[1] By 340°C, all of the H_2 was being removed.

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The next test was to see how long the oxygen on the catalyst would last. This was done by simply leaving the experiment in the configuration just described overnight. Figure 6 shows the results.
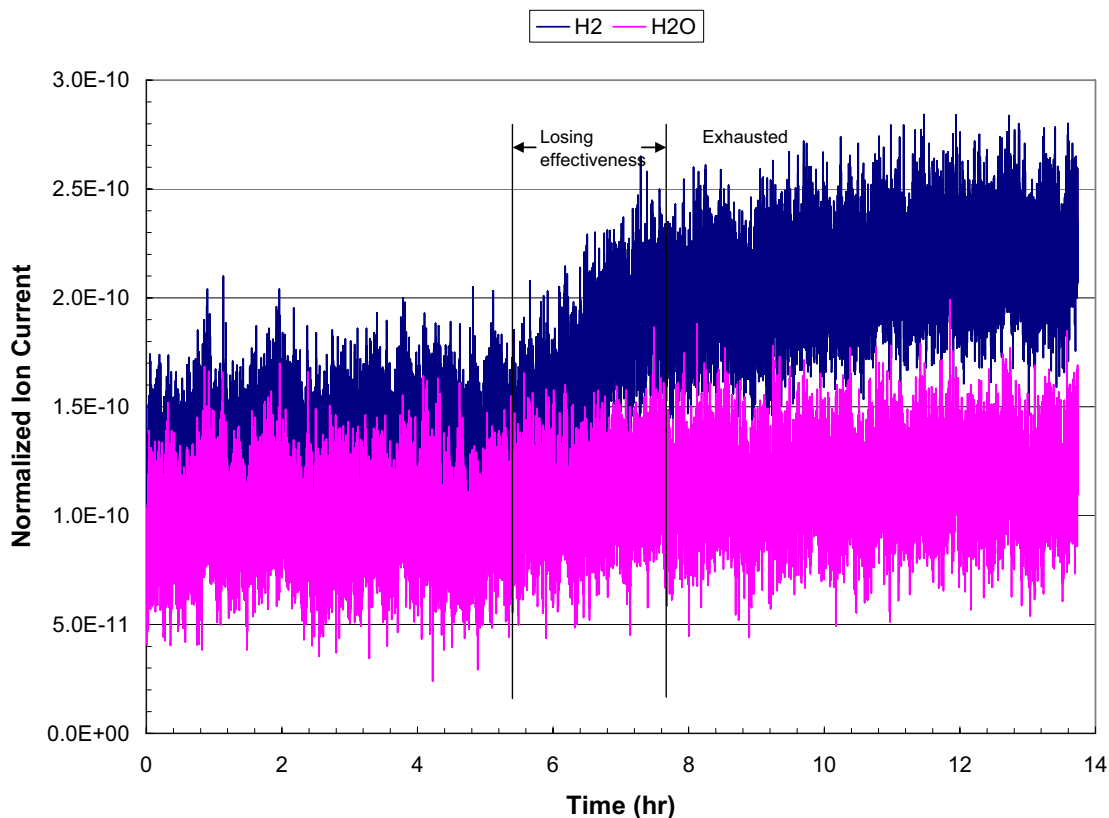

Figure 6. Catalyst exhaustion.

After 5.4 hours in this scan (6.67 hours total) with 2% H_2 in Ar flowing at 10.5 sccm at a temperature greater than 280°C, the catalyst began to lose efficiency. Until that time, it had been very effective in removing H_2 from the gas stream. The total number of moles of H_2 that passed through the catalyst before it began losing effectiveness was

$$6.67\,(hr) \times \frac{60\,(min)}{1\,(hr)} \times \frac{10.5\,(scc)}{1\,(min)} \times \frac{0.02\,(mole)}{2.24 \times 10^4\,(scc)} = 3.75 \times 10^{-3}\,(mole).$$

DISCUSSION

In the TMIST-2 experiment, there will be 6 modified MRB 500 equivalents. Four of these will be used to recover tritium in very low amounts from He-Ne mixtures. An upper bound estimate on the amount of tritium each may see is 1E-05 moles. Clearly, the capacity demonstrated above should be well sufficient to meet that need unless there is vastly more H than T in the system, which is highly unlikely. One other MRB 500 equivalent system, unit 5, will be used as a scavenger to process the flows from the first 4, one at a time, while the first 4 units are having their vials changed. Again, unit 5 should be easily able to handle the demand for oxygen placed

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on it. The final MRB 500 equivalent will be used to scavenge any tritium that may make it through a pair of Zr-Fe getter beds. An anticipated upper bound on the load it may see is

$$\frac{2 \times 10^{-3}\ Ci}{\left(m^3\right)} \times \frac{1\left(mole\right)}{5.8 \times 10^4\ \left(Ci\right)} \times \frac{1 \times 10^{-5}\ \left(m^3\right)}{1\left(sec\right)} \times 8.64 \times 10^6\ \left(sec\right) = 2.8 \times 10^{-6}\ \left(mole\right).$$

An ion chamber between the two getter beds will notify operators if the concentration there exceeds the 2 mCi/m^3 value used in this calculation.

After the catalyst bed tested in this experiment had stopped converting the H_2 to water, it was regenerated by passing room air over it at 475°C for 15 minutes. Following that process and restoring the H_2-carrying gas flow through the system, the mass-2 signal in the mass spectrometer was at background level, similar to that shown in Figures 4 and 5.

This test was not able to demonstrate that the water coming into the reaction from the bubbler could be counted on to undergo isotopic exchange and thus capture the tritium. It is probable that the isotopic exchange effect would be highly effective at capturing the small amount of tritium in the water vapor while effectively passing H_2 on in its place. That cannot be determined in this experiment without actually using tritium. Available time and laboratory resources do not admit of testing that process.

CONCLUSION

The MRB 500 stack monitor units modified with a CuO catalyst bed in a manner similar to the one we received for testing should be very satisfactory for use in the TMIST-2 experiment. If for any reason there is a need to regenerate the CuO, it may be simply done by passing air over the hot bed.

REFERENCE

1. G. R. Longhurst, February 2008, "TMIST-2 Transport Test," INL/EXT-08-13791, Idaho National Laboratory, Idaho Falls, ID 83415.