This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

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WSRC-TR-2004-00084

Analytical Method for Measuring Total Protium and Total Deuterium in a Gas Mixture Containing H_2, D_2, and HD via Gas Chromatography (U)

February 4, 2004

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Introduction and Summary

A new analytical technique has been developed that measures both total protium (H) and deuterium (D) in a gas mixture containing H_2, D_2, and HD. This new analytical technique uses a micro gas chromatograph (GC) with two molecular sieve columns. One column uses D_2 as the carrier gas and the other uses H_2 as the carrier gas. Laboratory tests have shown that when used in this configuration the GC can measure both total protium and total deuterium, each with a sensitivity of less than 20 ppm. This new analytical technique was developed as a result of a request from Tritium Facility Modernization and Consolidation (TFM&C) project to Instrumentation and Examination Systems (IES) to provide instrumentation to measure the protium and deuterium concentrations at several process points during initial testing of the new Hydrogen Tritium Thermal Cycling Absorption Process (HT-TCAP) columns in 233-H.

Discussion

HT-TCAP

The purpose of a HT-TCAP system is to separate tritium from other hydrogen isotopes to minimize environmental releases of tritium. A new HT-TCAP system was installed in 233-H to primarily separate protium and tritium of Z-Bed Recovery gases. Prior to introducing tritium into this new HT-TCAP system, TFM&C decided to test the system by substituting non radioactive deuterium mixtures for tritium mixtures. Two of the major process points of interest were the column raffinate and the column product.

During normal tritium operations, after several thermal process cycles, the column raffinate will contain pure protium, which may be released to the atmosphere via the stack, and the column product will contain pure tritium, which is transferred to hydride beds for storage. The limit for environmental releases of column raffinate is less than 5 atom ppm of tritium as HT, DT, or T_2. The column product quality for tritium is less than 0.1 atom % protium as HT, HH, or HD.

Ion Chamber

The instrument of choice to monitor the HT-TCAP process during normal tritium operations is an ion chamber. It is relatively inexpensive, simple to operate, and has sensitivity equivalent to less than 1 ppm. Therefore, monitoring for small quantities of tritium in the raffinate is relatively simple. However, for start-up test purposes, D_2 was substituted for T_2. Monitoring the column raffinate for small amounts of D_2 in pure H_2 presents a significant analytical challenge. Also, monitoring the column product for small amounts of H_2 in pure D_2 is a significant analytical challenge. To further complicate matters the HT-TCAP will also produce HD which may be in either the raffinate or product. Therefore, the analytical challenge for the test was to provide instrumentation to measure both total D in the column raffinate, and total H in the column product.

Instrumentation

A Residual Gas Analyzer (RGA), a Gas Chromatograph (GC), and a Helium Leak Detector were the instruments chosen to monitor the HT-TCAP process during the test. Each instrument has unique capabilities and limitations.

The RGA has 1 AMU resolution and can readily identify masses 2 (H_2), 3 (HD), and 4 (D_2) but isn't suited to quantify 5 ppm of HD in the presence of a large amount of H_2 or D_2 due to ionization interference issues and peak tailing.

The Helium Leak Detector has excellent sensitivity but must be tuned to detect either mass 3 or mass 4. It can't detect both simultaneously. It can quantify 5 ppm of either gas but if the leak detector is exposed to large quantities (greater than 500 ppm) for extended time the instrument will become saturated and will require several hours of pump-out time to adequately purge.

The GC has excellent sensitivity for hydrogen and can readily quantify 5 ppm. For H_2 detection the GC is typically configured with a molecular sieve column and argon carrier gas. In this configuration however, the GC cannot separate and quantify H_2, D_2, and HD from a mixture containing more than one of these gases. All of these hydrogen gases will co-elute and the result is a total hydrogen isotope measurement.

Used in conjunction, although cumbersome, these three instruments can trend the operation of the HT-TCAP process and demonstrate that it separates protium and deuterium. The instrumentation will show a decreasing concentration of deuterium in the column raffinate and an increasing concentration of deuterium in the column product. Final determination of HT-TCAP performance is accomplished by analyzing grab samples from the column raffinate and column product using the "Inert Lab" high resolution mass spectrometer in building 234-H.

New Analytical Method Development

Gas Chromatograph

The typical configuration of a GC to detect H_2 is a molecular sieve column with argon carrier gas and a thermal conductivity detector. The limitation of this configuration for testing the HT-TCAP process is the inability of the molecular sieve column to separate the hydrogen isotopes. (H_2, D_2, and HD). All of these species co-elute which makes it impossible, with a thermal conductivity detector, to identify and quantify each isotope. To solve this problem Instrumentation and Examination Systems conjectured that changing from argon carrier to H_2 carrier would allow the GC to mask the signal contribution of H_2, (in a sample containing both H_2 and D_2) and leave only the deuterium signal. Additionally, if D_2 were used as the carrier gas, it would mask the signal contribution of D_2 (in a sample containing both H_2 and D_2), and leave only the hydrogen signal. What was unknown was how this GC configuration would respond to the presence of HD in the sample mix.

The GC used for testing the HT-TCAP process and subsequently to develop this new analytical technique is a model M200 originally manufactured by Microsensor Technology Inc. and now manufactured by Agilent. This model GC has been applied to numerous processes and experimental work at SRS. It can be configured with two columns and two different carrier gases, which made it well suited for testing and developing this new analytical technique. Samples injected into the GC are analyzed simultaneously by the two columns.

Testing

A GC model M200 was configured with two molecular sieve columns. One column used H_2 carrier gas and the other column used D_2 carrier. Both columns were equipped with thermal conductivity detectors.

Initially gas mixtures containing (25%H_2, 75%D_2), (50%H_2, 50%D_2), and (75%H_2, 25%D_2) were analyzed. As anticipated each GC column displayed only one peak and this peak amplitude varied as predicted. The maximum height of the peak for the GC column with H_2 carrier gas was with the (25%H_2, 75%D_2) mixture and the minimum peak height was produced by (75%H_2, 25%D_2) mixture. This data meant that the peak represented D_2 concentration. The maximum height of the peak for the GC column with D_2 carrier gas was produced by the (75%H_2, 25%D_2) mixture and the minimum peak height was with the (25%H_2, 75%D_2) mixture. This data meant that the peak represented H_2 concentration. A three point calibration curve was generated for each GC column based on the area under the curve for each analysis.

Next, a test was performed with a mixture containing (25%H_2, 50%HD, 25% D_2) to determine how each column would respond to the presence of HD. The results were that the GC column with deuterium carrier gas reported a value of 50% H_2 and the GC column with hydrogen carrier gas reported a value of 50% D_2. In essence this GC configuration gave a measurement of the total amount of deuterium and the total amount of protium in the sample mixture. Various other mixes of (H_2, HD, D_2) were analyzed and each time values of total deuterium and total protium were correctly quantified. The sensitivity to both protium and deuterium was determined to be less than 20 ppm. This is significantly better sensitivity than the 234-H "Inert Lab" high resolution mass spectrometer which has a detection limit of 100 ppm for H_2 and D_2.

Data and Test Procedure

Enumerated and tabulated below are the test sequences and data from the development of this method.

1) The following partial pressure gas mixtures were made for use as calibration gases

   50%H_2 50%D_2
   75%D_2 25%H_2
   25%H_2 75%D_2

2) These gas mixtures were analyzed by the GC. The table below shows the analytical results. Each gas sample was analyzed three times.

GC Analysis Of H2 D2 Mixtures					
		Analysis # 1	**Analysis # 2**	**Analysis # 3**	**Average**
Mixture 50% D2 50% H2		(Area Counts Under Curve)			
Column A (H2 carrier Gas)	D2=	69,140,528	69,140,658	69,149,321	**69,143,502**
Column B (D2 Carrier Gas)	H2=	48,541,600	48,541,455	48,545,632	**48,542,896**
Mixture 75% D2 25% H2					
Column A (H2 carrier Gas)	D2=	100,414,040	100,464,512	100,593,056	**100,490,536**
Column B (D2 Carrier Gas)	H2=	24,483,564	24,507,014	24,551,368	**24,513,982**
Mixture 25% D2 75% H2					
Column A (H2 carrier Gas)	D2=	36,488,572	36,493,176	36,531,768	**36,504,505**
Column B (D2 Carrier Gas)	H2=	71,972,384	72,009,008	72,042,288	**72,007,893**

3) A calibration curve was generated for each column based on the area under each peak from each analysis.

   $D_2 = 7.813E\text{-}07x - 3.69$ x = Area Counts Under Peak
   $H_2 = 1.053E\text{-}06x - 0.904$ x = Area Counts Under Peak

4) The gas mixtures listed in step one were passed through a palladium diffuser to generate the following mixtures containing HD. These mixtures were also analyzed by the "Inert Lab" high resolution mass spectrometer in 234-H to provide a traceable analysis.

Diffuser Input 25%D2 75%H2	H2	HD	D2
Mass Spec Analysis of Output	56.67%	36.69%	6.64%
Diffuser Input 75%D2 25%H2	H2	HD	D2
Mass Spec Analysis of Output	6.82%	36.97%	56.22%
Diffuser Input 50%D2 50%H2	H2	HD	D2
Mass Spec Analysis of Output	26.36%	48.73%	24.89%

5) The gas mixtures containing HD were analyzed by the GC. The table below shows the analytical results.

GC Analysis of Diffuser Output	
Mixture Analyzed	GC Analysis
H2 (26.36%), HD (48.73%), D2 (24.89%)	
Column A (D2 carrier Gas)	H2=51.36%
Column B (H2 Carrier Gas)	D2=48.51%
Mixture Analyzed	
H2 (6.82%), HD (36.97%), D2 (56.22%)	
Column A (D2 carrier Gas)	H2=26.12%
Column B (H2 Carrier Gas)	D2=73.70%
Mixture Analyzed	
H2 (56.67%), HD (36.69%), D2 (6.64%)	
Column A (D2 carrier Gas)	H2=75.87%
Column B (H2 Carrier Gas)	D2=23.94%

6) ½ of the HD value from the Mass Spec Analysis was added to either the H_2 or D_2 value. These calculated values were then compared to the GC analysis.

Mass Spec Analysis	1/2 HD + (D2 or H2)	GC Analysis
D2=24.89%		
H2=26.36%	1/2 HD+D2 = 49.25%	D2=48.51%
HD=48.73%	1/2 HD+H2 = 50.72%	H2=51.36%
D2=56.22%		
H2=6.82%	1/2 HD+D2 = 74.70%	D2=73.70%
HD=36.975%	1/2 HD+H2 = 25.30%	H2=26.12%
D2=6.64%		
H2=56.67%	1/2 HD+D2 = 24.99%	D2=23.94%
HD=36.69%	1/2 HD+H2 = 75.01%	H2=75.87%

7) To determine the limit of detection of this analytical technique for D_2, the gas mixture containing 6.82% H_2, 56.22%D_2, and 36.97%HD was incrementally diluted with H_2 and measured with the GC.

Test Data to Determine Limit of Detection

Dilution	Theroretical Values PPM	GC Analysis PPM
0	747,000	734,910
10	74,643	74,980
100	7,464	7,658
1001.0	746.4	776.5
10009.6	74.6	78.4
20038.0	37.3	39.8
40722.0	18.4	19.4
81688.2	9.2	8.2

Attached are the analysis reports from the "Inert Lab" mass spec in 234-H for the gases from the diffuser output.

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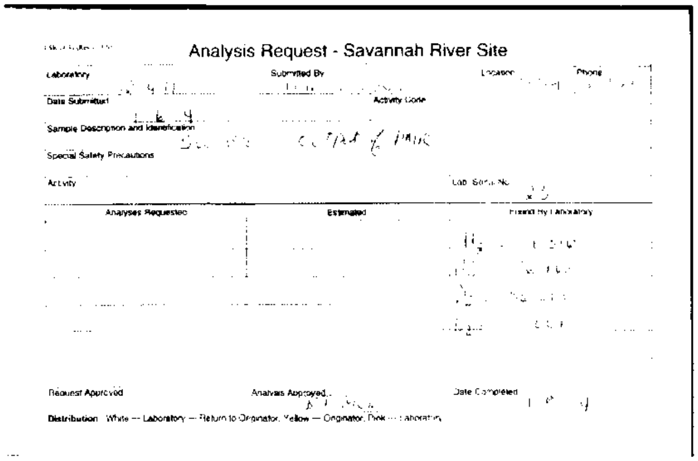
Attachment



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Submitted By [illegible]
Location [illegible]
Phone [illegible]
Date Submitted [illegible]
Activity Code
Sample Description and Identification [illegible]
Special Safety Precautions
Activity
Lab. Serial No. [illegible]

Analyses Requested	Estimated	Found By Laboratory
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		[illegible]
		[illegible]
		[illegible]

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Analysis Approved [illegible]
Date Completed [illegible]

Distribution White — Laboratory — Return to Originator, Yellow — Originator, Pink — Laboratory

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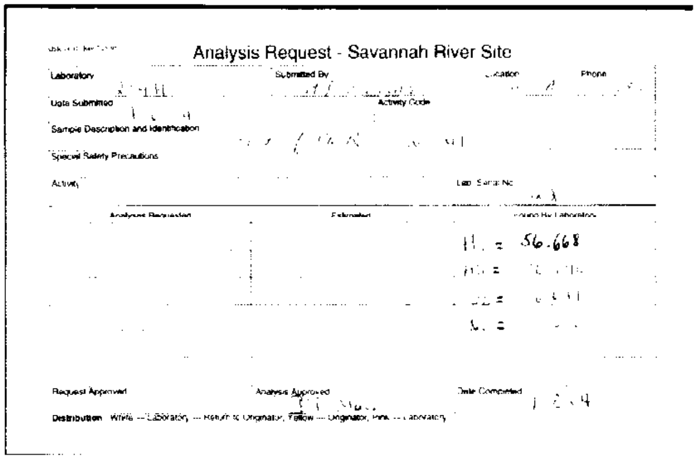

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Sample Description and Identification [illegible]
Special Safety Precautions
Activity
Lab. Serial No. [illegible]

Analyses Requested	Estimated	Found By Laboratory
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Request Approved
Analysis Approved [illegible]
Date Completed [illegible]

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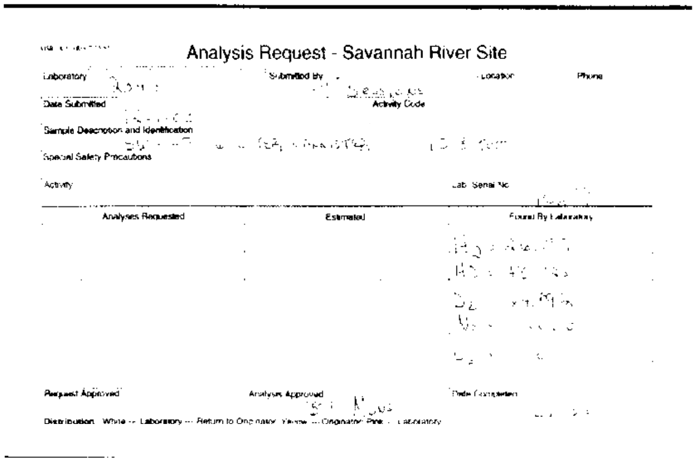

Analysis Request - Savannah River Site

Laboratory [illegible]
Submitted By [illegible]
Location
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Sample Description and Identification [illegible]
Special Safety Precautions
Activity
Lab. Serial No. [illegible]

Analyses Requested	Estimated	Found By Laboratory
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Request Approved
Analysis Approved [illegible]
Date Completed [illegible]

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