

AD-A123 070

METHOD FOR MEASURING ENRICHED LEVELS OF DEUTERIUM IN
SOIL WATER(U) COLD REGIONS RESEARCH AND ENGINEERING LAB
HANOVER NH J L OLIPHANT ET AL. NOV 82 CRREL-SR-82-25

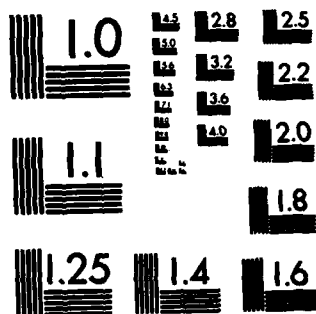
1/1

UNCLASSIFIED

F/G 8/4

NL

END
DATE
FILMED
2 83
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

ADA123070

THE UNIVERSITY OF CHICAGO PRESS
CHICAGO, ILL. 60607
PRINTED IN THE UNITED STATES OF AMERICA
BY THE AMERICAN BOOK CO. FOR THE UNIVERSITY OF CHICAGO
200 NORTH LAKE ST., PHILADELPHIA, PA. 19106

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Special Report 82-25	2. GOVT ACCESSION NO. AD-A123070	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) METHOD FOR MEASURING ENRICHED LEVELS OF DEUTERIUM IN SOIL WATER		5. TYPE OF REPORT & PERIOD COVERED
7. AUTHOR(s) J.L. Oliphant, T.F. Jenkins and A.R. Tice		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Cold Regions Research and Engineering Laboratory Hanover, New Hampshire 03755		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS DA Project 4A161101A910
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Cold Regions Research and Engineering Laboratory Hanover, New Hampshire 03755		12. REPORT DATE November 1982
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 15
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Deuterium Hydrogen isotopes Soil water		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report describes procedures for analyzing hydrogen isotope ratios. Hydrogen is separated from liquid water or soil water by reacting the water with heated uranium. An isotope-ratio mass spectrometer determines the atom % deuterium in the hydrogen to a precision of ± 0.0075 . Ways of upgrading the mass spectrometer to obtain better precision are also discussed.		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

PREFACE

This report was prepared by Dr. Joseph L. Oliphant, Research Soil Physicist, Thomas F. Jenkins, Research Chemist, and Allen R. Tice, Physical Sciences Technician, of the Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL). This work was conducted under the In-House Laboratory Independent Research Program (D.A. Project No. 4A161101A910). This report was technically reviewed by Dr. Harlan L. McKim and James Cragin, both of CRREL.

The authors thank Dr. Irving Freidman, USGS, Denver, Colorado, for providing advice on the design of the hydrogen generator and John Rand, Technical Services Division, CRREL, for assistance in selecting the heating unit most appropriate for use with the hydrogen generator.

CONTENTS

	Page
Abstract-----	1
Preface-----	11
Introduction-----	1
Methods of measuring the deuterium content of water-----	2
Preparing hydrogen gas-----	3
Determining D/H isotope ratios on the mass spectrometer-----	5
Calibration and results-----	10
Changes required for measuring natural abundance-----	11
Conclusion-----	11
Literature cited-----	12

ILLUSTRATIONS

Figure

1. Apparatus for preparing hydrogen gas samples from pure water and soil water----- 4
2. Gas inlet system for hydrogen isotope analysis----- 6
3. Mass 2 voltage vs balance panel reading for a sample with high deuterium content following a sample with low deuterium content----- 9

TABLES

Table

1. Ions from a mixture of H and D with H more abundant than D----- 7
2. Settings used during operation of Nuclide mass spectrometer for determining D/H ratios----- 8



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

METHOD FOR MEASURING ENRICHED LEVELS OF DEUTERIUM IN SOIL WATER

by

Joseph L. Oliphant, Thomas F. Jenkins and Allen R. Tice

INTRODUCTION

Naturally occurring hydrogen occurs as two isotopes. The nucleus of the atom of one isotope, protium, is made of a single proton; this isotope has an atomic weight of about 1 gram/mole. The other isotope, deuterium, has a nucleus made of one proton and one neutron and has an atomic weight of about 2 grams/mole. In this report, the symbol H will refer to the light hydrogen isotope (protium) and the symbol D will refer to the heavy isotope (deuterium).

The hydrogen in natural waters is made up of about 0.016 mole % deuterium (Kirshenbaum 1951), although this value varies considerably depending on the history of the water. Variation in the abundance of deuterium in a given sample is the result of the difference in atomic weights of deuterium and protium. Water containing two protium atoms, H_2O , has a molecular weight of about 18 grams/mole; water containing one deuterium and one protium atom has a molecular weight of about 19 grams/mole. Because of this difference in molecular weights, every time part of a sample of water goes through a phase change, fractionation of the deuterium content of the water takes place and one phase of the sample is enriched in deuterium and the other phase is depleted. For example, when part of a sample of water freezes, the ice phase is slightly enriched in deuterium content and the water phase is depleted, because the water containing deuterium has a slightly lower melting point (Posey and Smith 1957, O'Neil 1968, Arnason 1969). Also, when part of a sample of water evaporates, the vapor is depleted in deuterium and the remaining liquid is enriched because of a similar difference in vapor pressure (Kirshenbaum 1951).

Fractionation of deuterium by naturally occurring processes has made it possible to use deuterium content as a tracer to determine the source and history of some natural waters. Rain and snow are usually lowered in deuterium content by an amount depending on the source and history of the

water in the clouds. The average deuterium content of rain and snow varies from place to place depending on altitude, latitude and cloud history. Arnason (1977) has used this information to determine the sources of water in various hot springs in Iceland.

Usually lake water and groundwater will be richer in deuterium than rain water because of the partial evaporation that has taken place. Deuterium tracing has been used to determine the sources of water in various streams and lakes and to trace groundwater movement (Friedman and Redfield 1967, Thatcher 1967).

Deuterium is not radioactive, so it makes a very good nonabsorbing tracer and can be used safely in enriched levels in laboratory experiments and at natural and enriched levels in the field to trace water movement. A deuterium tracer has also been used in the laboratory to determine the rate of self-diffusion of the water in a soil (Kemper et al. 1964). This measurement yields information about the pore structure of the soil and the properties of the water affected by the soil matrix.

It is evident that the ability to measure hydrogen isotope ratios in water can be useful for studying water movement and properties in the field and in the laboratory. In this report we discuss a method developed at CRREL for measuring enriched levels of deuterium in soil water. First the various methods for measuring D/H ratios in water will be reviewed, and the reasons for choosing the isotope-ratio mass spectrometer method will be given. Then the apparatus for separating the hydrogen from the oxygen in water will be described and the experimental procedure outlined. The method of using the isotope-ratio mass spectrometer to determine D/H ratios will then be given along with an analysis of the accuracies and ranges of D/H ratios that can be measured on the present CRREL system. Finally modifications that must be made to this mass spectrometer so that it can accurately measure small differences in the amount of deuterium in natural waters will be listed.

METHODS OF MEASURING THE DEUTERIUM CONTENT OF WATER

Any difference in the physical properties of DHO and H₂O can be used as a basis for measuring the amount of deuterium in a water sample. Various methods that have been used were discussed by Kirshenbaum (1951). These methods include measuring densities of samples with a pycnometer, a float and a falling drop apparatus. Differences in refractive index,

freezing point, viscosity, vapor pressure, electrode potential and neutron absorption have also been used to measure water deuterium content. The density methods are fairly accurate and don't require a great deal of equipment to perform, but disadvantages include the relatively large amounts of sample required (0.1 - 1 mL) and the necessity of purifying the water. This is especially difficult to do with soil water while avoiding fractionation of the deuterium between phases. The other methods also require relatively large and solute-free water samples to obtain high accuracy. Measuring D/H ratios using the mass spectrometer requires only a very small amount of sample. Samples containing about 10 μ L of water each were used in this study. With care, samples of 1 μ L or even 0.1 μ L of water would be adequate for analysis.

Water is a polar molecule and is therefore very "sticky" and difficult to pump in vacuum systems. Direct introduction of water into a mass spectrometer causes large "memory" effects and difficulty in maintaining a vacuum in the system. Therefore, it is desirable to reduce the hydrogen in the water molecule to hydrogen gas and introduce this molecule in the mass spectrometer to determine D/H ratios.

Hydrogen gas samples have been prepared by reacting the water with hot magnesium or zinc, by equilibration of water with hydrogen gas of known isotopic composition, and by electrolysis of the water (Kirshenbaum 1951). Water electrolysis has the advantage that both oxygen and hydrogen can be collected for isotopic analysis, but it is difficult to completely convert the entire sample and thereby avoid fractionation. Equilibration with hydrogen gas requires considerable time and effort for each sample. Bigeleisen et al. (1952) found that uranium metal heated to between 400° and 700°C reacts very rapidly and completely with water, yielding uranium oxide and free hydrogen gas. Because of the convenience of this reaction, we used depleted uranium to prepare hydrogen gas samples for the mass spectrometer.

PREPARING HYDROGEN GAS

The apparatus for preparing hydrogen gas is shown in Figure 1. A sample of moist soil can be attached at A, or a microsyringe can be inserted at A' and a liquid sample introduced. At A there is a 1/4- in. swagelok fitting with a teflon sleeve. A small test tube containing the moist soil can be attached and the teflon sleeve swaged tight around the

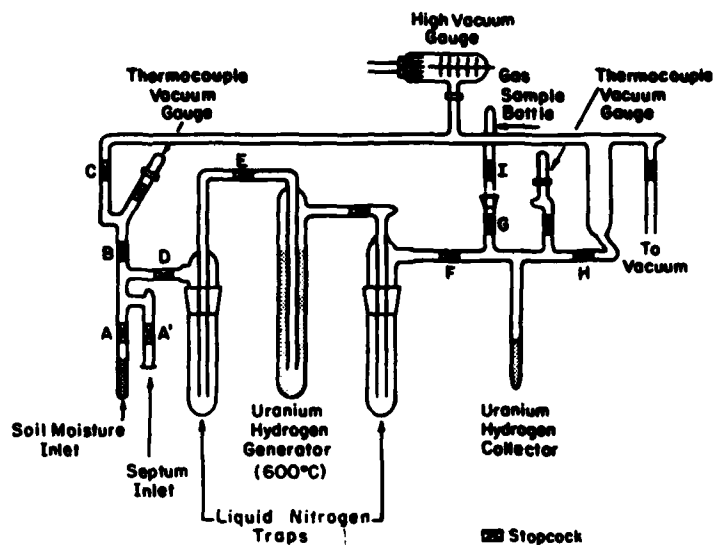


Figure 1. Apparatus for preparing hydrogen gas samples from pure water and soil water.

test tube to form an airtight seal. After the sample is either injected or attached, stopcocks C and E are closed and A' or A is opened. A Dewar flask containing liquid nitrogen is then placed around the left liquid-nitrogen trap, and the soil sample or septum inlet is heated with a hand-held heat gun. This causes the water to leave the septum inlet or soil sample and migrate to the liquid nitrogen trap. This migration can be monitored on the left thermocouple vacuum gauge. It is important that sufficient heat is applied to collect all of the water in the liquid nitrogen trap to avoid fractionation of deuterium in the sample. After all of the water is collected in the liquid nitrogen trap, stopcock C is opened (stopcock H must be closed) and A and A' are closed.

Any air introduced with the samples is then pumped away. This is also monitored on the left thermocouple vacuum gauge. It is important that air be removed before the sample contacts the heated uranium in the hydrogen generator because oxygen in the air (as well as from the water) would react with the uranium, greatly reducing the service life of the hydrogen generator. After the air has been removed, stopcock D is closed and E is opened. The Dewar containing liquid nitrogen is removed from the left trap, and the heat gun is used to heat the trap. This causes the water to vaporize and pass through the uranium hydrogen generator, which is heated by a surrounding furnace to about 600°C. The formation of hydrogen gas is indicated by the pressure rise on the right thermocouple gauge.

While the reaction in the hydrogen generator was taking place, we placed a Dewar containing liquid nitrogen around the right liquid nitrogen trap to collect any water that passed through the hydrogen generator without reacting. We never found water in this trap, so the reaction must have been completed in one pass through the hydrogen generator. The uranium hydrogen collector was placed in the system to remove and concentrate small samples of hydrogen gas from the large volumes of the liquid nitrogen traps and the hydrogen generator. Stopcock F could then be closed and the concentrated hydrogen gas driven into the gas sample bottle. For the 10- μ L samples we used, this concentration step was not necessary. The uranium hydrogen collector works because uranium hydride is formed at room temperature; at elevated temperatures the hydride breaks down and hydrogen gas is released. To prevent hydrogen from collecting, a heating mantle filled with sand was placed around the uranium hydrogen collector and kept at several hundred degrees centigrade. In the future a stopcock should be placed between the uranium hydrogen collector and the rest of the system, so that it can be closed when hydrogen concentration is not necessary.

After the hydrogen is generated, stopcock C and stopcock I on the gas sample bottle are closed, trapping a portion of the generated hydrogen in the gas sample bottle. This bottle is then removed from the system for use on the mass spectrometer. In preparation for the next sample, a new sample bottle is placed on the system, stopcocks H, G and I are opened, and this part of the system evacuated. Then stopcocks F and D are opened and the entire system is evacuated to a pressure of about 1×10^{-2} Pa. The complete preparation of one hydrogen sample takes about 20 minutes.

DETERMINING D/H ISOTOPE RATIOS ON THE MASS SPECTROMETER

A Nuclide isotope-ratio mass spectrometer (Nuclide 6-60-RMS) was used for determining the D/H isotope ratio. This was originally obtained to measure $^{15}\text{N}/^{14}\text{N}$ isotope ratios, so the gas inlet system had been modified (Jenkins and Quarry 1978) (Fig. 2). Two samples can be contained in the system at one time, and the gas going to the mass spectrometer can be switched from one to the other. We ran the hydrogen samples sequentially, so only half of the gas inlet system was used. The gas sample bottle is first attached as shown in Figure 2, stopcocks C' and B' are opened, and the system is evacuated up to stopcock J' on the sample bottle. Stopcock B' is then closed and C' opened. Manipulating stopcock E' and the air

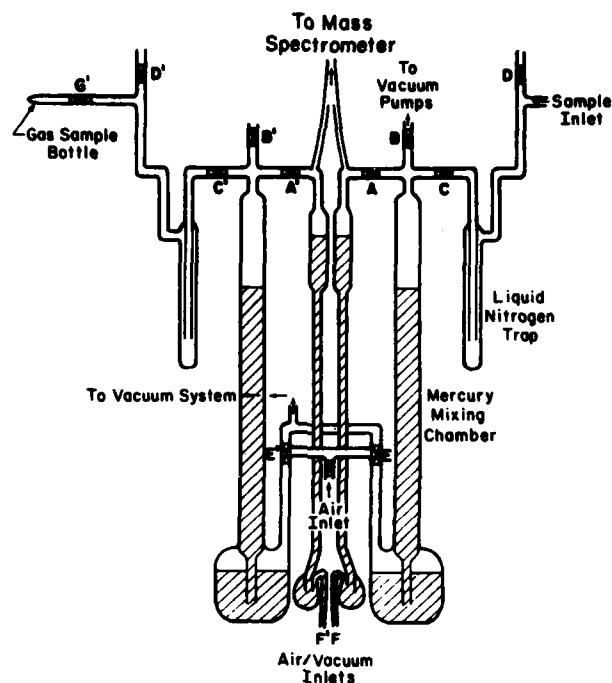


Figure 2. Gas inlet system for hydrogen isotope analysis.

inlet causes the mercury in the mixing chamber to rise and fall, preventing any fractionation of hydrogen isotopes in the sample. Stopcock C' is then closed and A' opened. The level of mercury in the mixing chamber is then raised and that in the mass spectrometer inlet is lowered, driving the hydrogen gas into the mass spectrometer inlet. Stopcock A' is then closed and the level of mercury in the mass spectrometer inlet is adjusted to obtain the desired pressure. Ion source pressures in the range of 10^{-4} to 10^{-5} Pa were used.

Inside the mass spectrometer the hydrogen entering the ion source is directed through an electron beam. Electrons collide with a portion of this hydrogen, transferring large amounts of kinetic energy. If the energy transferred exceeds the ionization potential, an electron will be ejected from the hydrogen molecule, forming a positive ion. For mixtures containing more H isotope than D isotope, the ions shown in Table 1 form. The ions are then accelerated by an electric field, producing a stream of ions with nearly constant energy. This stream of ions is dispersed into a mass spectrum by a magnetic field. In the Nuclide dual-collector, isotope-ratio mass spectrometer, selected ion masses are focused simultaneously on separate collector plates. The currents from these collector plates pass

Table 1. Ions from a mixture of H and D with H more abundant than D. (From Kirshenbaum 1951.)

Ion	Mass	Intensity	Pressure dependence*
H^+	1	weak	$a_1 p + b_1 p^2$
H_2^+	2	very strong	$a_2 p$
D^+	2	very weak	$a_3 p + b_3 p^2$
H_3^+	3	weak	$b_4 p^2$
HD^+	3	weak	$a_5 p$
D_2^+	4	very, very weak	$a_6 p$
H_2D^+	4	very, very weak	$b_5 p^2$
HD_2^+	5	very, very weak	$b_6 p^2$
D_3^+	6	very, very weak	$b_7 p^2$

* The symbol p is the hydrogen gas pressure in the ion source, and a_1 through a_6 and b_1 through b_7 are constants.

through separate resistors; the voltages across these resistors are measured and compared in a bridge circuit to obtain the relative amounts of the two collected masses. For measuring samples with small amounts of deuterium, the mass 2 and mass 3 ion intensities are compared. The pressure dependencies of ion formation (Table 1) show that at very low pressures, the mass 2 intensity is mostly H_2^+ and the mass 3 intensity is mostly HD^+ . For samples containing mostly deuterium, the mass 3 and mass 4 intensities made up mostly of HD^+ and D_2^+ , respectively, should be compared. For samples containing intermediate amounts of deuterium, the best accuracy is obtained by comparing the mass 2, 3 and 4 intensities.

The mass spectrometer instrument settings used for measuring D/H isotope ratios are shown in Table 2. To make a measurement, the instrument is set, and both electrometers are zeroed while set on 0.1 V full scale. The source divider is tuned to maximize the mass 3 ion intensity on electrometer A using the fine-level control and the difference knob. The ratio switch is then turned on and the instrument adjusted to maximize the ratio of the mass 3 to mass 2 current by turning the fine magnet-current control. This adjustment is made with both electrometers set on

Table 2. Settings used during operation of Nuclide mass spectrometer for determining D/H ratios.

Emission Regulator Settings

Ion deflector - off
Filament current - 530
Emission current - set to give 200 μ A target current
Electron accelerating potential - 500
Repeller to shield - 50 (to give 40 V)
Trap to shield - 0

Ion Accelerating Potential

Power - on
Coarse - 970
Fine - 500

Magnet Regulator

Power - on
Magnet current (coarse) - 2.00
Magnet current (fine) - 5.00

Ion Pump Power Supply

Output voltage - 4.7 kV
Protect - 10^{-3} Pa

Control Panel

Source power - on

0.1 V full scale and with very low hydrogen pressure inside the mass spectrometer. The instrument is adjusted before a sample is introduced into the mass spectrometer by using the background levels of mass 3 and mass 2.

After the instrument is calibrated, a sample is put into the mass spectrometer at a pressure high enough to give a mass 2 or major isotope voltage of 7-10 V with the balance panel set at 0.0000. The balance panel is then adjusted to zero out the mass 2 voltage, and the balance panel reading is recorded. The hydrogen gas inlet pressure is then lowered incrementally, and the balance panel reading required to zero the mass 2 voltage is recorded at each pressure. In preparation for the next sample,

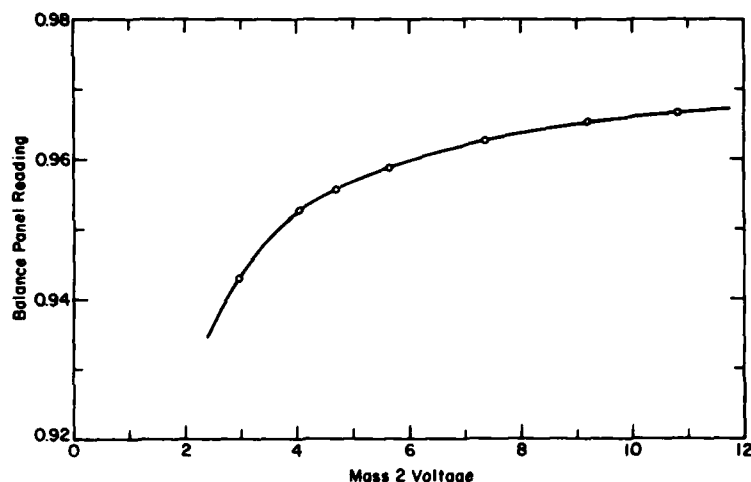


Figure 3. Mass 2 voltage vs balance panel reading for a sample with high deuterium content following a sample with low deuterium content.

the excess sample in the mass spectrometer inlet is pumped out; with practice, we reduced the cycle time for each sample to about 15 minutes.

Figure 3 is a plot of the mass 2 voltage vs the balance panel reading for a typical sample. The balance panel can be adjusted from readings of 0.0000 to 0.9999. The scale in Figure 3 has been greatly expanded to emphasize that this curve is relatively flat at high mass 2 voltages, but the readings are lower at low mass 2 voltages. We found that the shape of this curve depends on the difference in deuterium content of successive samples. For the sample shown in Figure 3, the previous samples had a much lower deuterium content. For samples measured after previous samples of a higher deuterium content, the curves are again flat at high pressures, but the readings are higher at low pressures. The reason for this is that the ion pumps are not as good as they should be in removing hydrogen from inside the mass spectrometer; as the pressure falls, more of the previous sample is mixed in with the current sample measurement. To minimize this memory effect, samples of about the same deuterium content were run in sequence, and for each sample the balance panel reading at a high pressure, giving a mass 2 voltage of about 10 V, was used to calculate the D/H isotope ratio.

The sample deuterium content can be approximated as follows. First, because the resistance in the major isotope collection electrometer is 1/20 of that in the minor isotope electrometer, the balance panel reading is divided by 20. This gives the ratio of mass 3 ions to mass 2 ions col-

lected. If it is assumed that the mass 3 ions are all HD^+ and the mass 2 ions are all H_2^+ and that the ionization and collection efficiencies inside the mass spectrometer are equal for the two masses, the atom % deuterium can be calculated by the equation

$$\text{Atom \% D} = \frac{100}{2 I_2/I_3 + 1} \quad (1)$$

where I_2/I_3 is the ratio of mass 2 ions to mass 3 ions collected. The maximum reading on the balance panel is 0.9999, so the minimum value of I_2/I_3 is about 20, giving a maximum atom % D that can be measured of 2.44%. For samples with higher deuterium contents, both the mass 2 and mass 3 ions must be focused sequentially on the major isotope collector by varying the current to the spectrometer electromagnet and recording the maximum voltage obtained at each mass. A ratio of these voltages determines the value of I_2/I_3 .

CALIBRATION AND RESULTS

Table 1 shows that the assumption that the mass 2 and mass 3 peaks are entirely H_2^+ and HD^+ , respectively, is never entirely correct. Also, minor variations in the slit settings and internal geometry of the mass spectrometer make the collection efficiencies for mass 2 and mass 3 ions unequal. Therefore, to obtain accurate results, standard samples must be prepared, the deuterium contents measured, and the unknown samples compared with these samples. Two standards were made up by carefully weighing small amounts of 99.8% D_2O and mixing them with weighed amounts of natural distilled water. These two standards had deuterium contents of 0.1149 and 0.4900 atom %. Each day that unknown samples were run, each of these standards was also run. A plot was then made of the true standard value vs that calculated from eq 1. The equation of the line joining the two standard values on this plot was then determined. This equation has the form

$$y = a x + b \quad (2)$$

where y is the true standard value, x is the value calculated from eq 1 and a and b are constants. Values of x obtained for the unknown samples were used in eq 2 to determine the values of y , the atom % D in these samples.

The precision of this method was determined by running the same unknown sample on five days. A mean value of 0.2706 ± 0.0075 atom % deuterium was obtained. This degree of precision is adequate for samples having

enriched amounts of deuterium but is inadequate for measuring small differences in the natural abundance, which is only about 0.016 atom % deuterium in natural waters.

CHANGES REQUIRED FOR MEASURING NATURAL ABUNDANCE

While the procedure for measuring deuterium contents of enriched samples was being perfected, one of the authors (T. Jenkins) visited Don Marshall at Nuclide Corporation. They discussed the changes required to provide precise D/H ratio measurements at natural abundance levels. The following recommendations were made:

- 1) Switch from ion pumps to diffusion pumps for evacuating the mass spectrometer. Ion pumps have been found to release hydrogen from previous samples. This change should greatly reduce the sample memory problem in the mass spectrometer.
- 2) Change the sample inlet on the mass spectrometer to air-operated, Nupro SS4BK 1/4-in. swagelock switching valves. This will make it possible to switch rapidly between unknown and standard samples for comparison.
- 3) Install stainless capillaries (3 ft long and 0.006-0.007 in. I.D., swagelocked in place) between the sample inlet and the interior of the mass spectrometer.
- 4) The slit widths on both the source and collector were originally set for ^{15}N analysis and need to be widened for D/H analysis. The source slits should be set at 0.036 in. and the collector slits at 0.055 in.
- 5) Purchase a new electrometer head with a resistor specifically for D/H natural abundance work.

The cost of these modifications was estimated to be \$5,000-10,000 for hardware alone, so a specific need for making natural abundance measurements must be shown to justify the changes.

CONCLUSION

A method for analyzing D/H ratios of both adsorbed soil waters and liquid water samples has been demonstrated. The hydrogen preparation apparatus that reacts water with heated uranium to form hydrogen and uranium oxide has been shown to work efficiently and to give quantitative results. With the mass spectrometer in its present configuration, sufficiently precise analyses are readily obtainable for enriched tracer

work. If very precise natural abundance measurements of deuterium are needed, a method of reconfiguring the mass spectrometer for these more precise measurements has been given.

LITERATURE CITED

Arnason, B. (1969) Equilibrium constant for the fractionation of deuterium between ice and water. Journal of Physical Chemistry, vol. 73, p. 3491-3494.

Arnason, B. (1977) Hot groundwater systems in Iceland traced by deuterium. Nordic Hydrology, vol. 8, p. 93-102.

Bigeleisen, J., M.L. Perlman and H.C. Prosser (1952) Conversion of hydrogenic materials to hydrogen for isotopic analysis. Analytical Chemistry, vol. 24, p. 1356-1357.

Friedman, I. and A.C. Redfield (1967) Application of deuterium analyses to the hydrology of the lakes of the Grand Coulee, Washington. In Isotope Techniques in the Hydrologic Cycle (Glen E. Stout, Ed.). Richmond, Virginia: William Byrd Press, Inc., p. 77-80.

Jenkins, T.F. and S.T. Quarry (1978) Methodology for nitrogen isotope analysis at CRREL. CRREL Special Report 78-8.

Kemper, W.D., D.E.L. Maasland and L.K. Porter (1964) Mobility of water adjacent to mineral surfaces. Soil Science Society of America Proceedings, p. 164-167.

Kirshenbaum, I (1951) Physical Properties and Analysis of Heavy Water. New York: McGraw-Hill Book Company, Inc.

O'Neil, J.R. (1968) Hydrogen and oxygen isotope fractionation between ice and water. Journal of Physical Chemistry, vol. 72, p. 3683-3684.

Posey, J.C. and H.A. Smith (1957) The equilibrium distribution of light and heavy waters in a freezing mixture. American Chemical Society Journal, vol. 79, p. 555-557.

Thatcher, L.L. (1967) Water tracing in the hydrologic cycle. In Isotope Techniques in the Hydrologic Cycle (Glen E. Stout, Ed.). Richmond, Virginia: William Byrd Press, Inc., p. 97-108.

EN

DAT
FILM

2-8

DTI