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MASS SPECTROMETRIC DETERMINATION OF DEUTERIUM IN WATER

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MASS SPECTROMETRIC DETERMINATION OF DEUTERIUM IN WATER

INTRODUCTION

A method for the determination of deuterium in water was necessary to support a research problem being conducted by members of the Metabolism Unit of Radiological Sciences Department (1). The problem is to determine whether or not preferential retention of hydrogen isotopes (H_2O, D_2O, T_2O) takes place in various organ tissues of mice. This requires a precise determination of the concentrations of protium, deuterium, and tritium oxides, which are present in the water samples obtained by dehydrating the required tissues.

SUMMARY

The method developed and described in this report is suitable for precision determinations of deuterium oxide in protium oxide for concentrations ranging from 0.01 to 99.9 mole per cent D_2O. Tritium oxide interferes if its concentration is high enough to be detected on the mass spectrometer.

THEORY

Direct analysis of water samples in the mass spectrometer is unsatisfactory because the adsorption and retention of water on the surfaces of the analyzer assembly cause cross contamination of samples. To prevent this cross contamination, the water is either converted to hydrogen or equilibrated with hydrogen to obtain a gaseous sample having the same isotopic composition, or one related to that of the water sample by known laws. The gas is then analyzed for protium and deuterium.

Various methods for obtaining the hydrogen sample are described in the literature (2, 3, 4). Direct reduction of the water to hydrogen gas by electrolysis, or by an active metal, such as calcium or zinc, is possible. The main objection to this method is the extreme care necessary to insure reduction of the entire sample to molecular hydrogen so that no fractionation can take place. Another method is one in which hydrogen or deuterium gas is equilibrated with the liquid sample and aliquots of this gas analyzed for isotopic composition. This equilibration method was the one chosen for this work.

THE EQUILIBRATION METHOD FOR PREPARING THE GAS SAMPLES

The equilibration requires the introduction of a hydrogen atmosphere into the vapor phase above the water sample (H_2O, HDO, D_2O) and an interchange of gaseous hydrogen with the hydrogen isotopes in the vapor until a dynamic equilibrium is attained. Fischer and Potter (4) derived a general equation for the mole per cent of deuterium in water in terms of the concentration of D_2, HD, and H_2 in the equilibrated gas. At 25°C, this is:

$$\text{Mole per cent deuterium in water} = \frac{1290\ (D_2) + 194\ (HD)}{3.87\ (HD) + 12.9\ (D_2) + (H_2)}\ .$$

This equation may be further simplified for samples having low deuterium concentrations, in which event practically all of the deuterium will be found in the HD molecules; therefore, the contribution from D_2 molecules is negligible. The following equation applies for low concentrations of deuterium:

$$\text{Mole per cent D in water} = \frac{194 \frac{(HD)}{(H_2)}}{1 + 3.87 \frac{(HD)}{(H_2)}} .$$

DETERMINATION OF THE ISOTOPIC CONCENTRATIONS OF THE GAS

This method of measuring the isotopic concentrations may, of course, be used for any protium, deuterium mixture, but the comments here will be confined to the gas sample obtained from the equilibration method.

The protium deuterium mixture may be measured conveniently on an isotope ratio mass spectrometer. A Consolidated-Nier Model 21-201, which uses a viscous leak gas inlet system, has been employed for the analyses reported herein. Although the instrument is designed to give optimum performance when comparing an m/e value of 45 with an m/e value of 44, it is adaptable to ratio measurements at other m/e values by using a reference voltage, which may be set equal to the output voltage produced by the isotope of highest concentration. The mass ratios used in a hydrogen-deuterium analysis are m/e = 3 to m/e = 2 and m/e = 4 to m/e = 2.

In the interpretation of the isotope ratio data, certain corrections must be made. Consideration must be given to:

1. Contributions to the 3 peak by other ions.
2. Contributions to the 2 peak by D_2^{++}.
3. Mass discrimination in the gas flow.
4. Water vapor contamination of the spectrometer.
5. Hydrogen memory between samples.

There will be contributions to the m/e = 3 peak from two sources: 1) the HD from the water used in the experiments, and 2) the formation of H_3^+ ions in the analyzer. The first contribution to the 3 peak is determined by running suitable "blanks" on the water used in the analyses. The formation of H_3^+ is due, presumably, to collison of an ion with a neutral molecule ($2H_2^+ + H_2 \longrightarrow 2H_3^+$). The concentration of the H_3^+ is proportional to the square of the pressure of the gas in the region of ionization, whereas the concentration of the HD^+ is proportional to the pressure; hence, the contributions to the m/e = 3 peak may be determined empirically from a plot of pressure vs. magnitude of the 3 peak covering the desired range of inlet pressures. The contribution of D_2^{++} to the m/e = 2 peak can be determined by proper calibration. In this work with low deuterium samples, the effect is negligible.

Since the flow of gas in the region of ionization in the spectrometer is molecular, a mass correction must be applied to the ratios to correct for differences in pumping rates of gases away from the region of ionization. The calculation of this correction from theory has been confirmed by experimental work.

The presence of water vapor in the spectrometer presents an added problem in that excessive memory effects are produced and dilution of the sample by the water vapor results. Therefore, it is important to carefully freeze out the water in the gas samples just prior to the analysis. There are also memory effects due to adsorption of the hydrogen isotopes on the walls of the analyzer which produce significant errors in subsequent analyses if the isotope ratio of the adsorbed hydrogen differs from that of the sample being analyzed. Other sources of error are circuit drift

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and air contamination, both of which can be made negligible by careful attention to technical details.

A method of analysis which obviates these errors and the necessary corrections is the graphical method suggested by Kirshenbaum (Ref. 3, p. 238). This method involves equilibrating a series of standards and analyzing the equilibrated gas on the mass spectrometer. The plot of 3 peak/2 peak vs. mole per cent deuterium is used as a calibration curve.

EXPERIMENTAL

Equilibration Time Studies

Before the procedure could be completely developed, it was necessary to ascertain the length of time the sample should be equilibrated. The use of a catalyst, such as platinum oxide, was found to be necessary, and Smith, Hutchinson, and Judson (Ref. 3, p. 206) have shown that the addition of a peptizing agent and shaking the sample during the equilibration both tend to increase the rate of equilibration. The addition of a peptizing agent, such as maleic anhydride, keeps the platinum oxide in suspension for longer periods of time, and thus hastens the attainment of equilibrium. The data in Table I substantiate this. An equilibration period of three hours was selected for analysis in this low D_2O range.

TABLE I

EQUILIBRATION TIME OF A STANDARD WATER SAMPLE
MADE UP TO 0.18 MOLE % DEUTERIUM WITH COLUMBIA RIVER WATER AND D_2O

Time	Mole % Deuterium	Method
1 hr. 30 min.	.161	Shaking with peptizing
2 " 30 "	.185	" " "
1 " 40 "	.079	No shaking, no peptizing
2 " 40 "	.174	" " " "
3 " 40 "	.178	" " " "
4 " 15 "	.187	" " " "

Graphical Method

A series of standard water samples were made up using Columbia River water and D_2O (furnished by the Biological Research group), covering the range of deuterium concentrations expected in the unknowns (0.01, 0.02, 0.05, 0.10, 0.20, 0.50, 1.00, and 2.00 mole per cent). These samples were equilibrated with hydrogen, and the gas was analyzed to obtain a working curve of the 3 peak/2 peak ratio vs. mole per cent deuterium. The zero intercept of this plot was confirmed by equilibrating hydrogen with Columbia River water and analyzing the gas. Thus, the correction for contributions to the ratio of the 3 peak to 2 peak from the deuterium in the natural water and H_3^+ was determined empirically to be 0.000410 at an inlet pressure yielding a 15 volt 2 peak. The D_2O was analyzed by the equilibration method and found to contain 97.6 mole per cent deuterium. Table II is a tabulation of the standards analyses, giving the factor which may be used in computing the mole per cent of deuterium in a sample.

TABLE II

FACTORS OBTAINED FROM STANDARD MIXTURES

$$\text{Factor} = \frac{\text{Mole \% } D_2O \text{ in Standard}}{(\text{Ratio 3 peak/2 peak}) - 0.000410}$$

Standard Mole % D_2O Added	Vol. of Sample	Factor
0.00974	0.5 ml.	150.7
"	1.0	159.7
"	1.0	154.7
0.0487	0.5	140.2
"	1.0	144.8
0.0974	0.5	151.7
"	1.0	149.1
"	1.0	150.1
"	1.0	152.9
0.195	1.0	146.5
"	1.0	147.8
"	1.0	146.6
0.487	1.0	146.0
"	1.0	150.9
"	0.5	144.3
1.901	1.0	150.9
"	1.0	148.9
	Ave.	149.2 ± 11.2*

*Error of a single measurement, 99% confidence level.

Calculations

Samples should be run in the order of increasing deuterium concentrations and with each series of unknowns analyzed, a standard of approximately the same concentration must be equilibrated and analyzed. The reproducibility of the standard is a measure of the accuracy of the analysis based on the standard. Since the Biological Research group anticipates analyzing the pre-injection solution prior to the analyses of the solutions obtained from the various organs of the animal, it is not necessary that an absolute value be obtained. The graphical method can be made as accurate as the standards which make up the standard curve, and the following mathematical check is made on each series of unknowns using the standard which is analyzed with this series to ascertain the validity of the results obtained:

$$\frac{\text{mole per cent } D_2O \text{ in standard}}{\text{ratio 3 peak/2 peak of standard - ratio 3 peak/2 peak of water}} = 149.2 \pm 11.2.$$

The value obtained in the above check must conform to the established value within ± 11.2, which is the precision (99% confidence limits) as determined in this experimental work. If the check is out of control, the sample must be re-analyzed and another standard check made. Calculations of per cent deuterium in samples are made with the same equation.

The analyzer tube must be baked for a 30-minute period prior to the analysis of a series of samples to reduce the memory effect to an allowable level; for this reason, also, the samples are analyzed in ascending values of concentration. From the limited number of analyses made on standards and unknowns to date, the precision limits tabulated in Table III were obtained.

TABLE III

PRECISION ATTAINED IN ANALYSIS OF D_2O IN WATER BY THE GRAPHICAL METHOD

Mole % D_2 Range	Precision of single determination, Dev. from mean (99% C.L.)
0.01-0.05	± 20%
0.051-0.075	± 10%
0.0751-0.1	± 7%
0.101-3.00	± 3%

General Equation Method

The following equations express the corrected ratios of concentrations in the gaseous phase where (H_2), etc., represent mole per cent in that phase.

(1) Corrected $(HD)/(H_2)$ ratio $= f_{HD}\left[\left(\frac{3\text{ peak}}{2\text{ peak}}\right)_{sample} - \left(\frac{3\text{ peak}}{2\text{ peak}}\right)_{water}\right]$

(2) Corrected $\frac{(D_2)}{(H_2)}$ ratio $= f_{D_2}\left[\left(\frac{4\text{ peak}}{3\text{ peak}}\right)_{sample}\left(\frac{3\text{ peak}}{2\text{ peak}}\right)_{sample}\right]$

where $f_{D_2} = 0.742$ and $f_{HD} = 0.865$ are the factors for D_2 and HD determined for the mass spectrometer.

The ratios in equation (1) may be subtracted directly because the hydrogen pressure is kept constant for all analyses.

The corrected values are then inserted into the general equation to give the concentration in the aqueous phase.

$$\text{Mole \% deuterium} = \frac{1290\frac{(D_2)}{(H_2)} + 194\frac{(HD)}{(H_2)}}{3.87\frac{(HD)}{(H_2)} + 12.9\frac{(D_2)}{(H_2)} + 1}$$

Procedure

Place the sample of water consisting of 0.5 to 5 ml. in a 30 ml. equilibration flask. Add 6 mg. of dry platinum oxide and 2 mg. of dry maleic anhydride and outgas the sample by freezing it in a dry ice bath and then evacuating the flask. Re-melt the sample and then repeat the outgassing procedure at least twice. Finally add dry hydrogen gas to the flask to approximately atmospheric pressure and allow the sample to equilibrate at a constant temperature of 25°C with continuous shaking for at least three hours. After equilibration, attach the flask to the

mass spectrometer manifold, freeze the water with a dry ice bath, and immediately admit a portion of the gas to the manifold, adjusting to a constant inlet hydrogen pressure, as read on the output meter. Measure the 3/2 and 4/2 ratios according to the standard operating procedure for the Consolidated-Nier isotope ratio mass spectrometer, as outlined in the Operator's Manual. For samples containing more than 3.0 mole per cent deuterium, calculate the concentration using the general equation.

$$\text{Mole \% } D_2 = \frac{1290 \frac{D_2}{H_2} + 194 \frac{HD}{H_2}}{3.87 \frac{HD}{H_2} + 12.9 \frac{D_2}{H_2} + 1}$$

For samples containing less than 3.0 mole per cent deuterium, use the graphical method to calculate results. In this case, omit the determination of the 4/2 peak ratio and use only the 3/2 peak ratio. Run three aliquots of the sample and a standard sample containing approximately the same deuterium concentration as the sample simultaneously. The maximum deviation of the three measured ratios (corrected for water blank) must not be more than ± 7% of the average.

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