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THE DETERMINATION OF DEUTERIUM AND TRITIUM IN EFFLUENT WASTEWATER
BY PULSED NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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ABSTRACT

A pulsed nuclear magnetic resonance (NMR) procedure was developed for the quantitative determination of deuterium and tritium in radioactive, effluent, wastewater to aid in the design of an efficient combined electrolytic/catalytic exchange system for the recovery of these hydrogen isotopes. The deuterium and tritium NMR signals were observed at 9.210 and 45.7 MHz, respectively.

Ten different effluent water samples were analyzed for deuterium and tritium to establish base-line data for the preparation of standard reference samples. The hydrogen isotope concentrations ranged from 0.11 to 2.40 g deuterium and from 2.0 to 21.0 mg tritium per liter of processed sample.

The standard deviation of the hydrogen isotope determinations is ± 0.017 g deuterium and ± 0.06 mg tritium per liter of processed effluent water. In the future, the effectiveness of specially prepared and analyzed (calorimetry) effluent samples as tritium standards will be investigated.

INTRODUCTION

A knowledge of the deuterium and tritium content of effluent wastewater is important in the design of an efficient system for extracting these valuable hydrogen isotopes. Not only will recovery of these isotopes reduce the cost of future procurements of these rare and expensive constituents (deuterium, 0.00154 atom % natural abundance, \$168 per gram; tritium, 0.00000 atom %, \$11,000 per gram), but will also prevent contamination of the environment with radioactive tritium. The system selected to accomplish this recovery is based on a combined electrolytic/catalytic exchange (CECE) process in which tritium is concentrated as T_2O by exchange with

the protium in H_2O . Because deuterium competes with the tritium for the protium in water, it is necessary to know the concentration of deuterium and tritium in the feed water in order to design an efficient system for their extraction. The exchange takes place because tritium and deuterium oxides are thermodynamically more stable than H_2O . The enriched water (D_2O) is electrolyzed and the tritium and deuterium gases are separated by cryogenic distillation. To determine the deuterium and tritium content of the feed water, a pulsed nuclear magnetic resonance (NMR) spectroscopic technique was selected because its detection limit (approximately 2 ppm for tritium and 100 ppm for deuterium with multiple scanning) met the levels requested without converting the sample from liquid to gas, which would be required for either mass spectrometry or gas chromatography.

EXPERIMENTAL

A Bruker B-KR 323a 4-100 MHz pulsed wide-line NMR spectrometer, a Varian V-4013A 12-in. iron core magnet, and a Nicolet Model 1074 Instrument Computer were used for this analysis. Absorption spectra were not used in the present analysis because the spectrometer system is not equipped to perform high-resolution Fourier Transform NMR on the wide-line free induction decay signals. The same analysis could be performed on a high resolution NMR system with greater ease, sensitivity, precision, and accuracy if one were available for studying radioactive materials in a radiation restricted area. The deuterium and tritium NMR signals were observed at 9.210 and 45.7 MHz and magnetic fields of 14,092 and 10,063 gauss, respectively. Because protium was used as a quantitative standard for the tritium determinations, it was necessary to collect the tritium and protium NMR signals under identical instrument conditions. Therefore, both tritium and protium were observed at 45.7 MHz, the upper limit for

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tritium at maximum magnetic field strength of 14,092 gauss.

Ninety-degree ($\pi/2$) pulse widths were used at all times (2.96, 3.10, and 21.6 μ sec for tritium, protium, and deuterium, respectively). These values will vary with transmitter power and tuning parameters. Pulse repetition times (1 sec for protium and 3 sec for tritium and deuterium) were adjusted to avoid saturation of the NMR signal due to long T_1 spin-lattice relaxation times. The T_1 relaxation times were not measured in our experiments. If they were determined, then the repetition time would have been adjusted to 5-10 times T_1 .

No stabilization of the magnet was used because magnetic field drift was insignificant over the collection time period (<1 hr) and because the trigger sequence of the NMR experiment and the Nicolet collection system were always synchronous. We now have provision for field stabilization (Mid-Continent Instruments Model FLS701 Magnetic Field Lock system).

Ten different effluent water samples (Table 1) were analyzed for their deuterium and tritium content to establish base-line data for the preparation of standard reference samples. The water drained from the effluent recovery system tanks contained solid debris and an organic phase which were removed prior to analysis. (These constituents are dealt with later.) A portion of the water drained from each tank was filtered to remove the solid debris and the filtrate was collected in a separatory funnel. The aqueous phase was separated and retained for the NMR analysis. A volume of 1.7 mL of this processed water was pipetted into 10-mm o.d., flat-bottomed, glass NMR sample tubes and sealed with pressure-tight plastic caps. Duplicate samples were prepared and analyzed. The NMR tubes were decontaminated and then sealed in specially designed cylindrical Teflon tubes for double containment of the tritium contaminated water.

A set of five standard deuterium samples, in the concentration range of the effluent water samples, was prepared for calibrating the instrument response to deuterium (Figure 1). The standards were prepared with pure D_2O in deionized, distilled water. The low levels of deuterium (~ 0.35 g/L) and tritium (~ 0.002 g/L) being determined prevented direct visual observation of the NMR signals during a single scan. Time-averaging of 64 and 1024 scans, respectively, of the deuterium and tritium resonances provided observable NMR signals with enhanced sensitivity of detection and increased signal-to-noise ratio, which improved the precision of the analysis. Even though tritium is more sensitive (Table 2) to NMR detection than deuterium, more scans were necessary for observing tritium because it was present in the water at lesser concentration (~ 100 times less) than deuterium. The sensitivity of detection was

Table 1' - NMR DEUTERIUM AND TRITIUM BASELINE DATA FOR EFFLUENT RECOVERY SYSTEM WASTE WATER.

Sample No.	Deuterium (mg/L)	Tritium (mg/L)
1	2340	19.7
	2390	20.6
2	390	11.4
	390	10.5
3	760	2.01
	770	2.01
4	340	1.95
	350	1.95
5	112	2.87
	109	2.87
6	200	2.87
	194	2.87
7	576	3.56
	565	3.56
8	694	3.44
	682	3.56
9	153	3.56
	159	3.44
10	312	2.30
	317	2.30

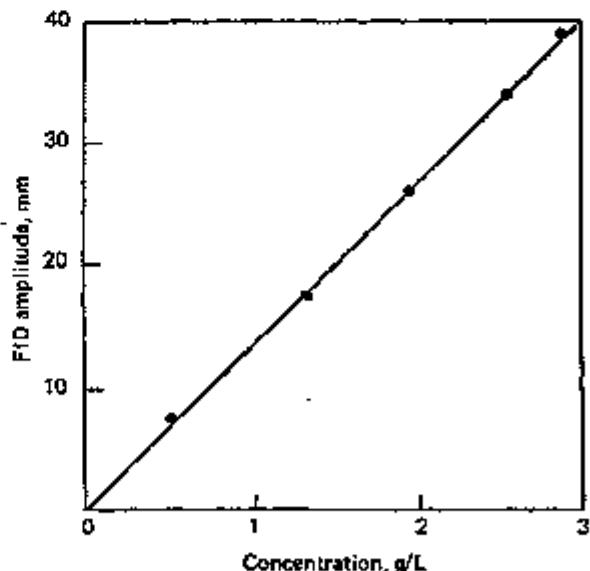


Figure 1 - Calibration curve for deuterium nuclear magnetic resonance response in standard D_2O samples.

Table 2 - NUCLEAR MAGNETIC RESONANCE PARAMETERS

Isotope	NMR Frequency (MHz)	Field Strength (gauss)	Relative Sensitivity
Protium	45.7	10,734	1.000
Deuterium	9.21	14,092	0.409
Tritium	45.7	10,063	1.07

also increased by setting the magnetic field for an off-resonance (Figure 2) free-induction-decay (FID) signal. This doubled the signal intensity by producing a negative signal equal in magnitude to the positive signal of an on-resonance FID signal. Recording of the off-resonance signal also reduces the errors due to small fluctuations in the rf reference phase, the radio-frequency transmitter, and the magnetic field intensity.

Instrument parameter adjustments (mainly, magnetic field strength, rf pulse width and reference phase, and electronic tuning of the rf transmitter power amplifier, receiver preamplifier, and rf coil tank circuit for maximum signal response) for the deuterium determinations were easily accomplished using standards prepared with pure D₂O in deionized, distilled H₂O. In the case of tritium, no standard is readily available for parameter adjustments and for plotting a standard curve. Presently, a low-level tritium-containing solid (PdRT/Al₂O₃) is being used for tuning the spectrometer, and H₂O standards are being used for constructing the analytical curve. The NMR responses of protium and tritium are almost identical, differing by a factor of 1.07 at constant frequency (Table 2). The hydrogen isotope concentrations ranged from 0.11 to 2.40 g deuterium and from 2.0 to 21.0 mg tritium per liter of processed water.

The standard curve is constructed by plotting the amplitude at time zero (see Figure 2) of the distance between the two lines drawn through the positive and negative peaks of the off-resonance FID signals (extrapolated back to time zero) versus the concentration of the reference samples. The concentration of the unknown samples is determined by interpolation from the standard curve or by using the equation from the least-squares, regression fit of the standards data. The validity of the extrapolation technique for obtaining the amplitude of the NMR signal related to the number of nuclear spins in the analytical sample is demonstrated in Figure 3. The on-resonance FID signal of deuterium follows, linearly, for at least 10 milliseconds, the off-resonance FID signal of the same sample. Tritium behaves similarly.

To place the hydrogen isotope determinations on a firm scientific basis, the NMR

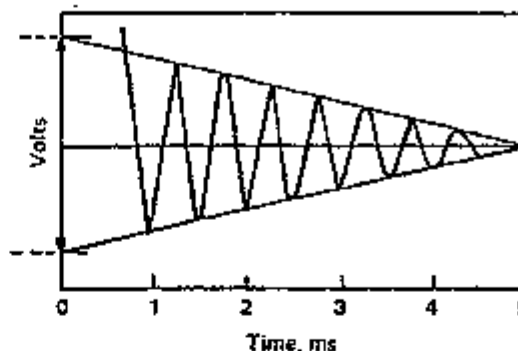


Figure 2 - Typical nuclear magnetic resonance free induction decay signal.

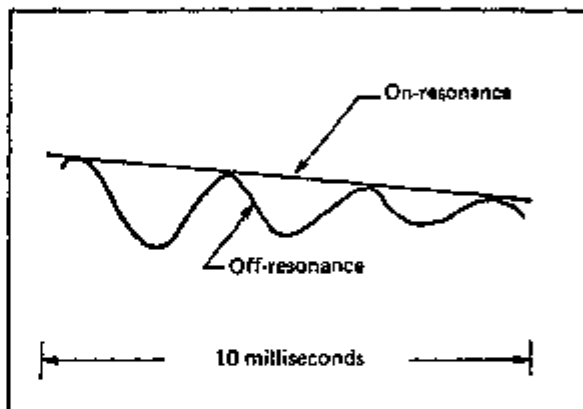


Figure 3 - On-resonance and off-resonance (decaying sine-wave) free induction decay signals of deuterium at 9.210 MHz.

line-shape for one of the deuterium FID decay signal was fit both to an exponential and a linear function (Figure 4). It was found that the decay signals within the 10 millisecond time frame fit the linear model much better than the exponential one. Therefore, the linear extrapolation technique is also substantiated mathematically by the linear regression fit.

RESULTS AND DISCUSSION

The results listed in Table 1 varied because the amounts of deuterium and tritium released by various laboratory operations were not constant with time. The tank that collects the ERS water is emptied only when it is full, which is once or twice a month depending on the demand put on the system. Also, since the laboratory atmosphere from which deuterium and tritium is recovered fluctuates in humidity from month to

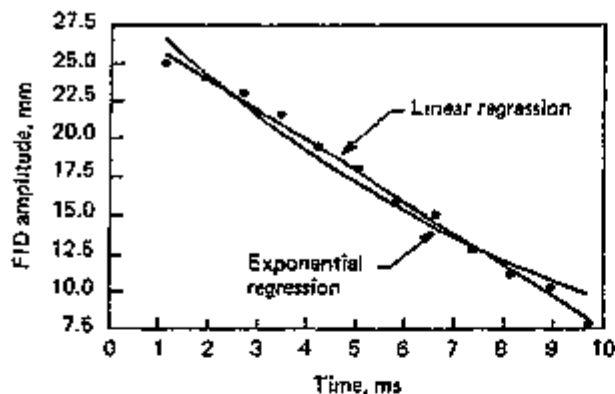


Figure 4 - Regression analysis of deuterium NMR data.

month, additional water is collected during the more humid months, and the hydrogen isotope levels appear to be lower than during the drier months. Therefore, a large number of samples obtained over a long period of time is needed in order to predict the range of deuterium and tritium in the ERS water. Ten sets of duplicate samples have been analyzed to date. Using the sum of the squares of the differences of ten duplicate analyses (10 degrees of freedom), the standard deviation of the hydrogen isotope

determinations is ± 0.017 g deuterium and ± 0.06 mg tritium per liter of processed effluent water. No definite accuracy statement can be made at this time because no absolute standard reference materials are available. It would be necessary to run samples of known deuterium and tritium contents in order to make statements of accuracy. In the future, the effectiveness of specially prepared and analyzed (calorimetry) effluent samples as tritium standards will be investigated. The effects of the solid debris and organic layer on the accuracy of the analyses will also be investigated, and the amount of deuterium and tritium in the organic phase will be determined.

CONCLUSION

The NMR method for determining deuterium and tritium in radioactive wastewater is relatively rapid compared to the alternative techniques of calorimetry, mass spectrometry, and gas chromatography. It requires less sample preparation, is nondestructive, and is precise (worst case, $1\sigma = 13\%$ relative standard deviation). The accuracy and sensitivity of the method can be improved tremendously by employing high-resolution NMR techniques and the high magnetic field intensities achieved by modern superconducting solenoids. The accuracy and precision of the present NMR analysis was sufficient to satisfy the requirements for the design of a system for the recovery of tritium and deuterium from radioactive wastewater.