

# DETERMINATION OF DEUTERIUM IN WATER SAMPLES BY NUCLEAR REACTION METHOD

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## Abstract

Ratio of D<sub>2</sub>O content to H<sub>2</sub>O content in water samples taken from the Karachaganak oil-gas deposit in Kazakhstan is measured by using D(d,p)<sup>3</sup>H nuclear reaction. Some underground cavities for gas store in this region were formed by nuclear explosions. Destruction of the cavities and penetrating of radionuclides to underground water can cause serious ecological troubles. Change of deuterium content in water is a reliable indicator of radionuclides migration and permits to prognosticate radionuclides contamination degree at regions remoted from the epicenter of explosions. The amount of deuterium in the samples was determined from the integrated yield of the D(d,p)<sup>3</sup>H reaction in relation to the <sup>16</sup>O(d,p)<sup>17</sup>O reaction. Obtained results are discussed.

## 1 INTRODUCTION

National Nuclear Center and the Institute of Nuclear Physics conduct works on radio-ecological monitoring of the region adjoining to underground gas store cavities. These cavities were formed as result of underground nuclear explosions. Destruction of the cavities and penetrating of radionuclides into underground water can cause serious ecological troubles. Deuterium, which had been formed during these explosions has high migration properties. Change of deuterium content in water is an indicator of radionuclides migration and permits to prognosticate radionuclides contamination degree at the regions remote from the epicenter of explosions.

Nuclear reactions D(d,p)<sup>3</sup>H and D(<sup>3</sup>He,p)<sup>4</sup>He are suitable for deuterium content analysis using accelerated particles within the energy range 0.1 – 2 MeV [1,2,3,4,5].

Cross section of the reaction D(<sup>3</sup>He,p)<sup>4</sup>He is about 700 mbarn and detection limit is 10<sup>13</sup> at/cm<sup>2</sup> at the energy of <sup>3</sup>He beam 700 keV [6]. Cross section of the D(d,p)<sup>3</sup>H reaction at the same energy of deuteron beam is about 100 mbarn. However, deuteron beam allows to measure oxygen simultaneously from the <sup>16</sup>O(d,p)<sup>17</sup>O reaction. This reaction can be used as internal standard of the analytical method such as concentration of oxygen in water is always constant. Then using ratio of yields of D(d,p)<sup>3</sup>H to <sup>16</sup>O(d,p)<sup>17</sup>O reaction for method calibration allows to avoid influence of beam current measurement errors and small

change of experimental geometry on accuracy of final results.

Standard water samples with different D/H ratio were prepared and measured for development of the quantitative method of analysis. Unknown samples were taken from the places, adjoining to underground cavities. These water samples were distilled and deep frozen before irradiation.

The experiment had been done at the deuteron beam energy 700 keV and detection angle 160°. These parameters were selected as compromise between maximum of D(d,p)<sup>3</sup>H reaction yield and minimum of <sup>16</sup>O(d,p)<sup>17</sup>O and <sup>12</sup>C(d,p)<sup>13</sup>C overlapping.

## 2 EXPERIMENT

### 2.1 Sample collection and preparation

The water samples were taken from two observing wells KN4 and KN12 which are located at the distance 50 and 300 m from the epicenter and their depth is 300 and 1100 m accordingly. These samples were stored in sealed plastic containers.

The water samples were frozen before irradiation. A cooling finger was installed into the target chamber and liquid nitrogen was used as coolant. The finger was cooled down before the target attaching. A small amount of water was shock frozen by introduction of the copper target holder into liquid nitrogen. In this way a layer of about 5 mm water could be frozen for about 3 minutes. Then the sample was placed inside the target chamber within one minute and evacuated up to vacuum ~ 10<sup>-6</sup> Torr by the turbo pump with capacity 500 l/s.

Relative method of analysis was used for determination of deuterium content in water samples. Therefore standard water samples with the different D/H ratio were prepared. The advantages of relative method are:

- Possibility of synthetic standards preparation;
- Non sensitivity of the method to small changes of experiment set-up and beam current on the target;
- Simplicity of results interpretation.

Preliminary analysis of the water samples has shown presence of dissolved carbon (CH group and carbon dioxide) and salts (concentration range from 11 to 46 g/l).

Content of matrix elements in unknown samples and in standards should be the same to ensure equal excitation conditions.

Moreover presence of significant amount of dissolved carbon provides high spectral background on the  $D(d,p)^3H$  line. Therefore water samples were distilled before irradiation.

## 2.2 Experimental arrangement

The experiments were carried out at the 1 MV tandem accelerator, model UKP-2-1 [7].

Deuteron beam was collimated by two 10 mm diameter diaphragms placed on the 3 m between them. Protons from the nuclear reactions were detected by a silicon surface barrier detector with a solid angle of 200 msr. Scattered deuterons were eliminated from spectrum by using of a 25  $\mu\text{m}$  Mylar absorber foil. The energy loss of protons in the Mylar foil was measured in separate experiment. The detector was placed on a movable console and could be installed with a high accuracy on any angle in range from  $0^\circ$  up to  $180^\circ$  in relation to ion beam axis.

A typical charged particles spectrum measured from frozen distilled water at the detector angle  $160^\circ$  and deuterons energy 700 keV is shown in Figure 1. Carbon peak is correspondent to surface carbon film formed as result of cracking of hydrocarbons from resident gas during irradiation.

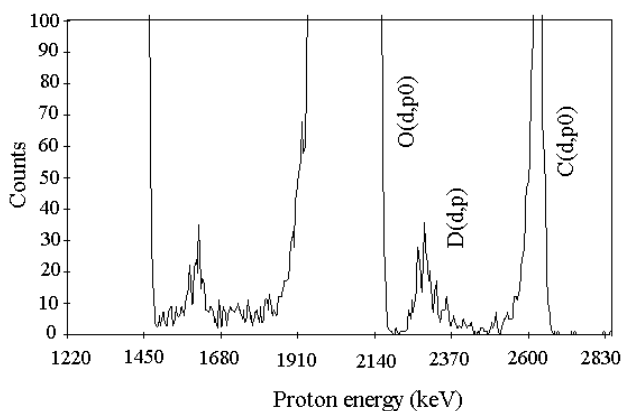


Figure 1: Charged particles spectrum measured from frozen distilled water at the detector angle  $160^\circ$  and deuterons energy 700 keV.

Rate of a carbon film deposit on the sample surface was reduced by increasing of deuteron beam current up to 150 – 180 nA (beam density  $\sim 3 - 4 \text{ nA/mm}^2$ ). Increasing of the beam current leads to raise of sublimation from the sample surface. Thickness of carbon layer depends on equilibrium conditions of these two processes.

Due to increased water sublimation from the sample surface, vacuum in the target chamber was about  $10^{-4}$  Torr.

Relative position of the proton groups at the energy scale depends on the deuteron energy and the detection

angle. So the best measurements condition can be selected by variation of these two parameters.

Calculation was made in classical approximation [8]:

$$E_{\text{out}} = K_1 E_0 [\cos\Theta + (K_2/E_0 + K_3 - \sin^2\Theta)^{1/2}]^2$$

where  $E_{\text{out}}$ ,  $E_0$  – protons and deuterons energy accordingly,  $\Theta$  – detection angle,

$K_1$ ,  $K_2$ ,  $K_3$  – constants, determined as:

$$K_1 = M_1 M_2 (M_1 + M_2) (M_3 + M_4),$$

$$K_2 = M_2 M_4 / M_1 M_3,$$

$$K_3 = Q [1 + M_1 / M_2] M_2 M_4 / M_1 M_3,$$

$M_1$ ,  $M_2$  – masses of deuteron and target nucleus accordingly,

$M_3$ ,  $M_4$  – masses of light and heavy products of reaction,

$Q$  – reaction energy.

Energy of protons for the nuclear reactions  $D(d,p)^3H$ ,  $^{12}\text{C}(d,p_0)^{13}\text{C}$  and  $^{16}\text{O}(d,p_0)^{17}\text{O}$  versus deuteron beam energy is shown in Figure 2.

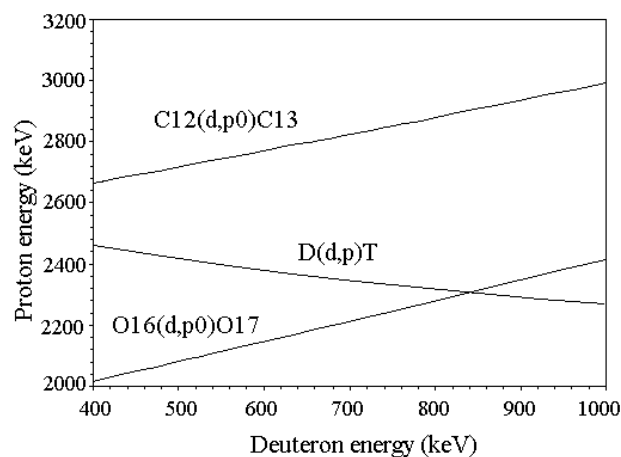


Figure 2: Energy of protons for the nuclear reactions  $D(d,p)^3H$ ,  $^{12}\text{C}(d,p_0)^{13}\text{C}$  and  $^{16}\text{O}(d,p_0)^{17}\text{O}$  versus deuteron beam energy.

Detection of protons at the angles less than  $90^\circ$  as regards to the beam axis allows to avoid carbon overlapping, but the method becomes extremely sensitive to the surface conditions of the sample. It strongly affects on accuracy and reproducibility of measurements.

At the detection angle  $160^\circ$  and energy of the deuteron beam 700 keV proton group from the  $D(d,p)^3H$  reaction is shifted to low-energy region where interference from  $^{12}\text{C}(d,p_0)^{13}\text{C}$  reaction is negligible. These conditions of experiment were selected for following measurements.

## 2.3 Results

Reproducibility test was made for evaluation of analytical accuracy of the method. The results of measurements of one and the same distilled water sample are presented in Figure 3. Relative standard deviation of D/O measurements does not exceed 6% in  $2\sigma$  confidence level (probability 95%).

The method of “standard addition” was used for determination of deuterium content in water samples. For this

aim, the standard samples with different D/H ratio within the range of added deuterium from 0 (distilled water) up to 0.05 at % had been prepared and measured. The standard samples were prepared by diluting of heavy water  $D_2O$  (99%) with distilled water. Calibration curve is shown in Figure 4.

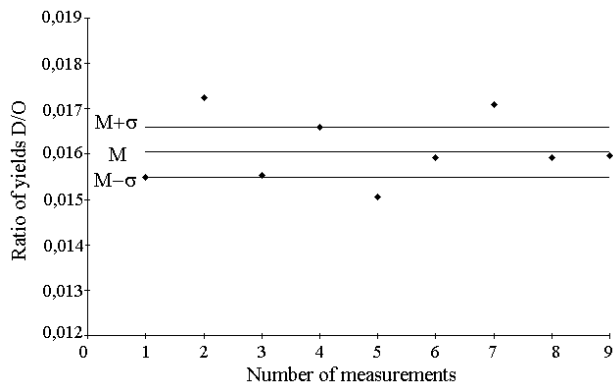


Figure 3: Ratio of yields D/O for the frozen distilled water.  $M$  – mean value of ratio D/O,  $\sigma$  - standard deviation.

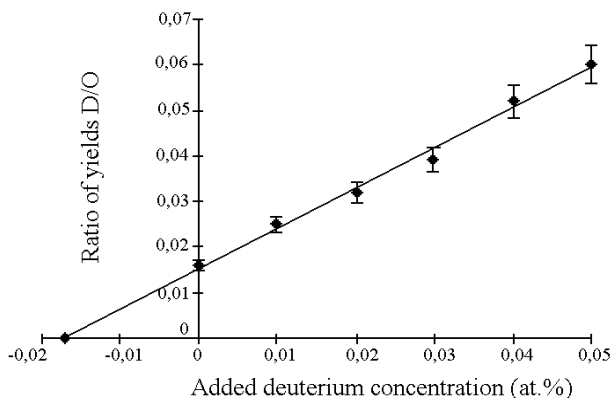


Figure 4: Deuterium calibration data.

Least-square fitting had been used here. Each data point corresponds to an integrated charge 0.2 C of deuteron beam. Axis X corresponds to added deuterium concentration and point 0 of this axis is related to distilled water. Background concentration of deuterium in the blank sample, calculated from calibration curve, is about 0.017% in relation to main isotope that corresponds to natural content of deuterium in water. This value coincides with other experimental data [3].

Six water samples taken from the observed wells were analysed. The results of the analysis are presented in Fig-

ure 5. No significant change of the deuterium to hydrogen ratio in comparison with distilled water was obtained.

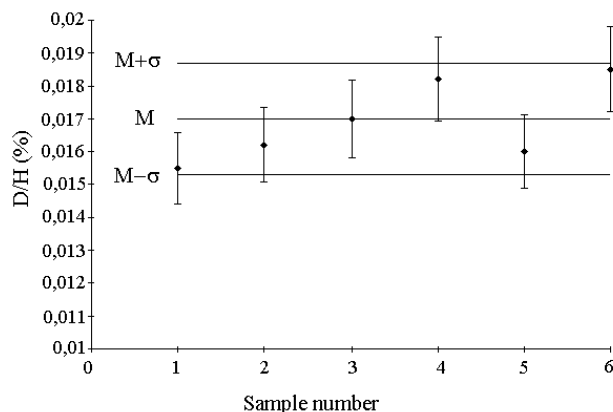


Figure 5: Measured deuterium concentration of D/H in the water samples taken from the observed wells. The well KN4: sample 1 – depth 30 m, sample 2 – depth 100 m, sample 3 – depth 272 m; the well KN2: sample 4 – depth 70 m, sample 5 – depth 500 m, sample 6 – depth 1000 m.

### 3 CONCLUSIONS

The range of deuterium content fluctuation in different water sources is  $D/H = 0.018 \pm 0.004\%$  [4]. It is considerably more than expected accuracy of the described method. However deuterium-hydrogen ratio must be more stable in normal condition in case of permanent monitoring of the same objects.

Thus excess of the constantly observed D/H ratio on  $3\sigma$  value (aprox. 10% relative) can be signal of possible ecological troubles.

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