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RADIOCARBON AND TRITIUM MEASUREMENTS IN WATER SAMPLES AND APPLICATION OF ISOTOPIC ANALYSES IN HYDROLOGY

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Abstract

The method of ^{14}C and ^{3}H measurements in water samples developed at "Rudjer Bošković" Institute are described. Radiocarbon which is dissolved in water in form of carbonates and bicarbonates is precipitated in form of $BaCO_3$. Carbon dioxide is released by acidification and converted into methane by reduction with hydrogen in presence of ruthenium catalyst. Water samples for tritium measurement are also converted into methane by the reaction of water with Al_4C_3 at 150°C. The activity of the purified methane is measured by a proportional counter. The counters for radiocarbon and tritium measurement are different construction, dimension and sensibility.

The results of tritium measurement in precipitation water in Zagreb from 1975 to 1979 are presented. The tritium concentration in the surface water of Plitvice Lakes and the results of ^{14}C and ^{3}H measurements of groundwater from Tripolitania are also presented.

Introduction

Radioisotopes tritium ^{3}H and ^{14}C are included in natural hydrological cycle. Measurements of concentration of these isotopes in natural waters (precipitation water, surface water and groundwater) are used as very successful methods in hydrology and related sciences (1,2). Both isotopes are formed in the upper layers of the atmosphere by interaction of thermal neutrons with nitrogen atoms. The ^{14}C atoms oxidize in atmosphere forming carbon dioxide while tritium is incorporated in water molecules. In this form ^{14}C and ^{3}H come to the surface of the earth in form of precipitation and atmospheric moisture and are included in the hydrological cycle. Part of precipitation flows in form of rivers into lakes and oceans, part evaporates into the atmosphere and part seeps into the groundwater.

Tritium is included directly into the structure of water form HTO molecules. ^{14}C isotope is found in the form dissolved carbonates and bicarbonates in water. Although precipitation water absorbs atmospheric carbon dioxyde containing ^{14}C atoms, radiocarbon of groundwater is not exclusively of this origin. By seeping through the soil, precipitation water disolves biogenic CO_2 whose specific activity is in equilibrium with activity of modern plants. If soil contains calcite ($CaCO_3$) it will be dissolved by precipitation water which contains carbonic acid. Following equation shows the chemical process:

$$x\,CaCO_3 + x\,H_2O + (x+y)\,CO_2 \rightleftharpoons x\,Ca(HCO_3)_2 + y\,CO_2 \qquad (1)$$

where x and y are molar concentrations of fixed and free carbonic acid.

The amount of dissolved calcium carbonate depends on dissolved CO_2. Dissolving occurs only at a few meters of depth in biologically active layer because the production of biologically active CO_2 ceases in greater depths as well as the dissolving of calcium carbonate. The dissolved calcite is millions years old and contains no radiocarbon. Theoretically, according to the equation (1), dissolved bicarbonates contain 50% of biological and 50% of anorganic (inactive) carbon. In this way the specific activity would be half of the activity in plants. Instead of expected 50%, the specific activity of bicarbonates in natural waters was found to be 65-100% of the activity of plants (3). The intial concentration of ^{14}C atoms is not equal in all aquifers because it depends on the complexity of physical and chemical processes occuring in water on its way through the soil. If the initial concentration of ^{14}C in water is known the remaining specific activity of ^{14}C in water determines the retention time, providing that there was no mixing of water in the aquifer. The maximum age of ~ 40 000 years can be measured ($t_{1/2}$ = 5730 years).

Tritium is an isotope with much shorter half-life, $t_{1/2}$ = 12.26 years. Measurements of tritium concentrations in precipitation, groundwater and surface water can show the interaction between the surface and the groundwater.

Measurement of ^{14}C and ^{3}H concentration in natural waters requires very sensitive technique of measurement because of low energetic β -particles (^{14}C, E_{max} = 156 keV, ^{3}H, E_{max} = 18 keV). In laboratory for measurement of low-level activities at "Rudjer Bošković" Institute, sample activities of ^{14}C and ^{3}H are measured in a gas proportional counter. Samples are converted to methane which is used as the counter gas (4,5). The background due to cosmic and gamma rays are reduced by shielding with lead and iron and by a mixture of boric acid and paraffine. Anticoincidence ring counter eliminates penetrating components of cosmic rays. The electronics is also a very sensitive part of the measuring system having low electronic noise, stable amplification and constant threshold. During ^{14}C and ^{3}H activity measurements a special care of contamination has to be taken. The procedure of ^{14}C and ^{3}H activity measurements includes the following operations: sample collection, chemical preparation of samples, measurements of the activity in the counter and statistical processing of data.

^{14}C measurement in water

The quantity of water for ^{14}C analysis depends on the concentration of dissolved carbonates and bicarbonates in water. It is determined according to the relations:

$$V = \frac{25\ 000}{\text{mg "A"}} \qquad (2)$$

where V is quantity of water (in liters) and mg "A" is the amount of carbonates and bicarbonates in milligrams per liter of water. The concentration of carbonates and bicarbonates is determined from the water alkalinity titration using pH = 8.0 for carbonate and pH = 4.5 for bicarbonate. Silicates, borates, hydroxides and other basic anions in water are also included in the titration. This causes an underestimation of the amount of a water sample. Therefore, at least 25% larger quantity of sample water has to be taken. Sample of water must not be contaminated during the collection with water from other horizons or with mud. Water must be collected in clean plastic containers rinsed with water sample.

Carbonates and bicarbonates are precipitated from water sample by adding saturated $BaCl_2$ solution after adjusting the pH of water to 8 by adding saturated NaOH solution (6). It was found that for quantitative precipitation of carbonates and bicarbonates dissolved in water, the same water sample has to be processed several times. After first precipitation the pH of solution is again adjusted to pH = 8 and further quantity of $BaCl_2$ solution is added. This procedure is repeated until the pH of water remains constant (after addition of $BaCl_2$ solution). The precipitation is speeded up by adding iron salts and a coagulating medium as Praestol. A 50 l plastic tank with plastic bottle fixed on the bottom is used for precipitation (fig. 1). The precipitation is carried out on site or in the laboratory, depending on the number of investigated samples, the distance from nearest facilities etc.

Carbon dioxide is released from the precipitate consisting mainly of barium carbonate by dissolving it in phosphoric acid. CO_2 is collected in a trap cooled by liquid air. The process is carried out in the atmosphere of nitrogen. Carbon dioxide is passed through $KMnO_4$ solution and through a cold trap at -80°C (fig. 2). The carbon dioxyde is converted into methane by reduction with hydrogen in the presence of ruthenium catalyst at 450°C (fig. 3). The methane is purified by passing

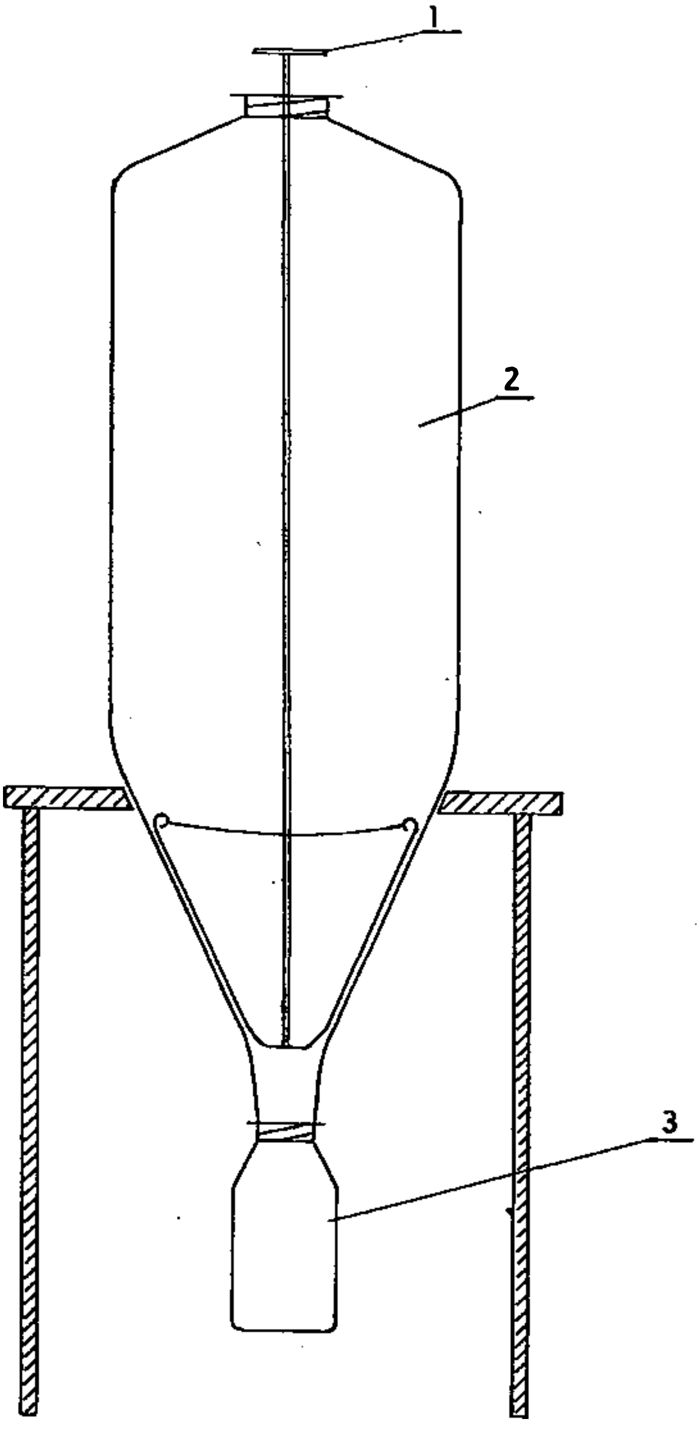

Fig. 1. Precipitator for carbonates from water.
1-stirrer, stainless steel; 2-50-liter plastic precipitator;
3-collection bottle..

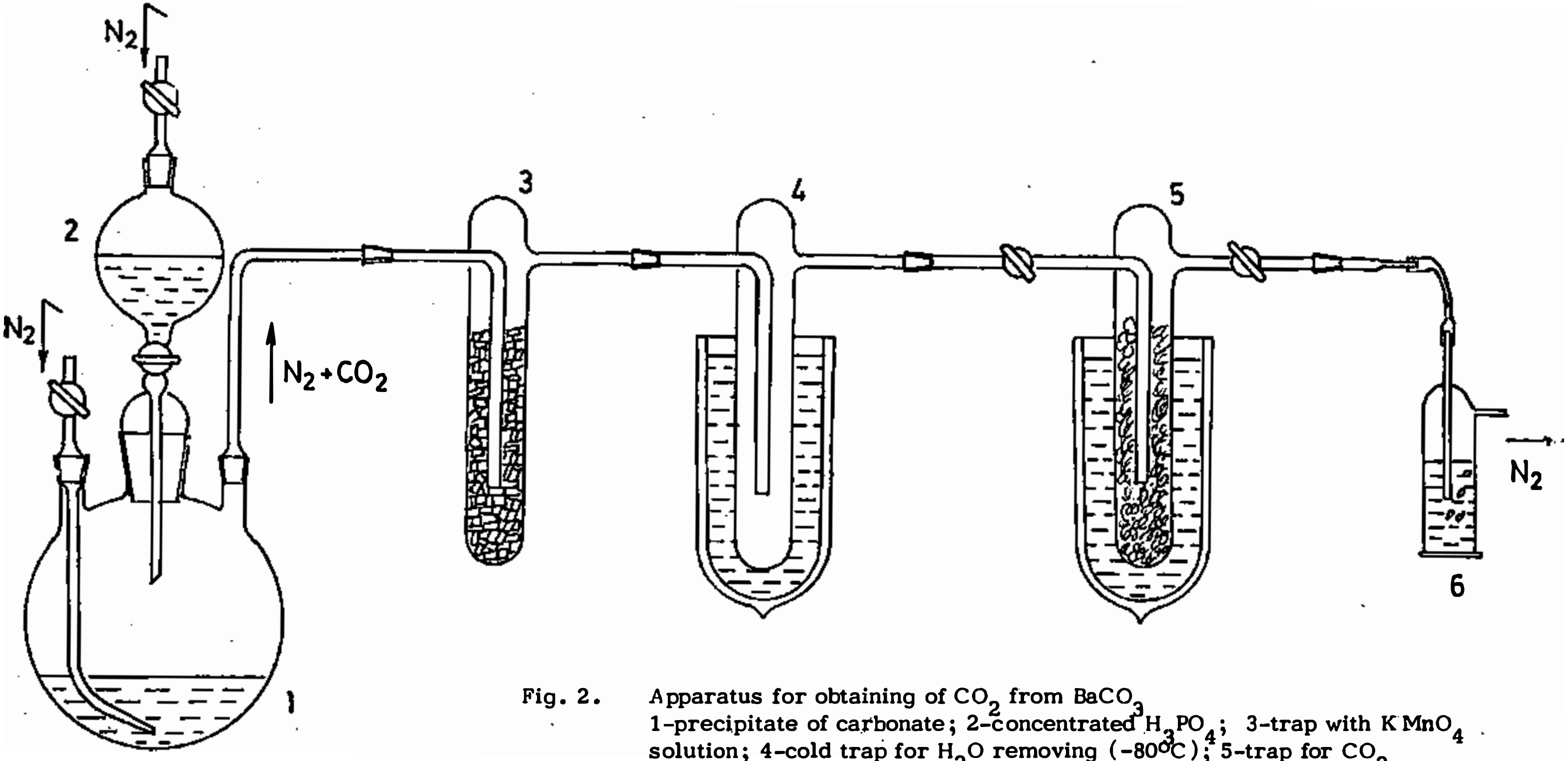

Fig. 2. Apparatus for obtaining of CO_2 from $BaCO_3$
1-precipitate of carbonate; 2-concentrated H_3PO_4; 3-trap with $KMnO_4$ solution; 4-cold trap for H_2O removing (-80°C); 5-trap for CO_2 collecting (temp. of liquid air); 6-bubbler.

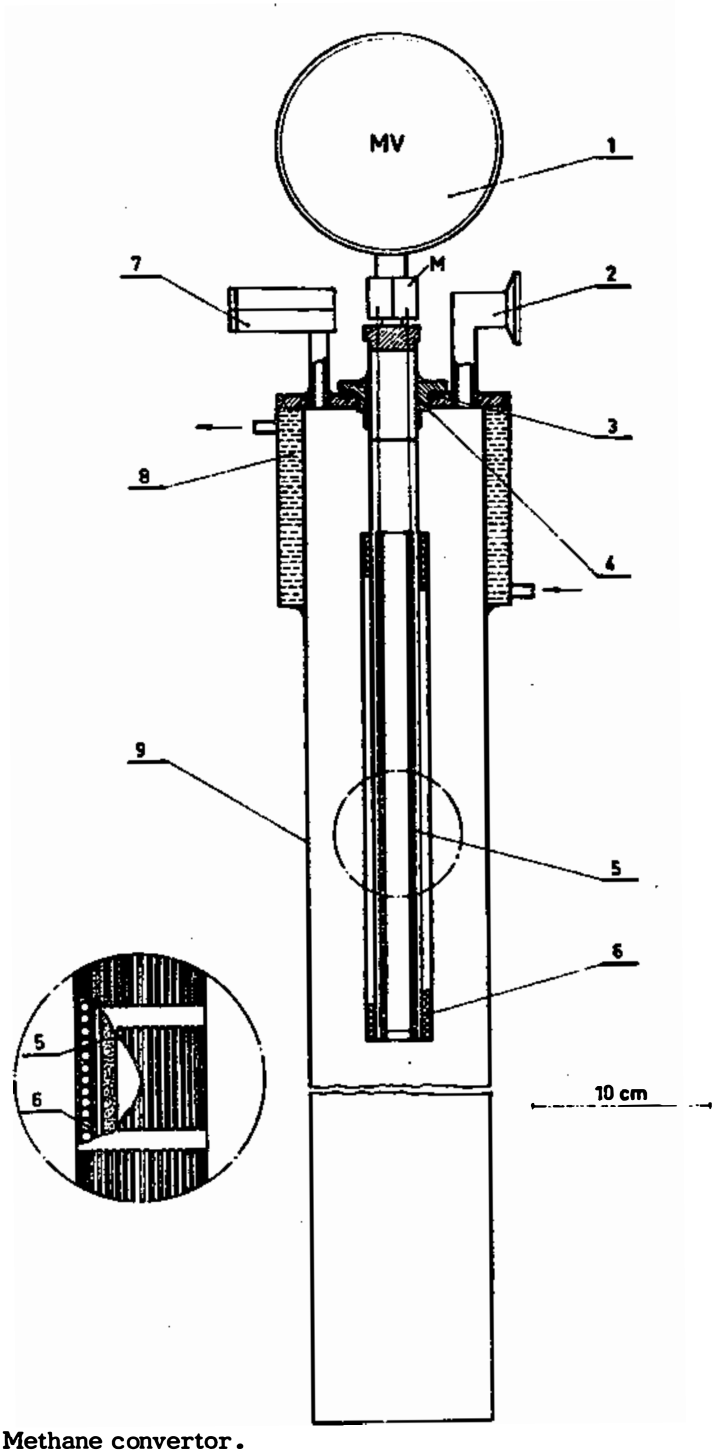

Fig. 3. Methane convertor.

1-pressure gauge; 2-vacuum pump flange; 3-Viton 0-ring; 4-catalyst holder; 5-heater; 6-catalyst; 7-H_2 and CO_2 inlet valve; 8-cooling coil; 9-stainless steel tank.

through a column filled with copper turnings heated to 700°C, followed by sodium hydroxide on asbestos and magnesium perchlorate absorbers.

The activity of the purified methane is measured in the proportional counter (4). The volume of the counter is 1.13 liters and the working voltage is 4500 V. The counter is filled with methane to 2.00 atmospheres.

The electronics is also an essential part of the measuring system. It consists of a preamplifier and an amplifier, a single-channel analyzer, an anticoincidence unit which eliminates coincident pulses, two high voltage supplies, a scaler and a printer. The anticoincident counts from the central counter are printed out on a tape every 20 minutes. The results of the measurements are statistically processed on an electronic computer.

Measurement of tritium concentration in water

Water samples for tritium measurements are also converted to methane. The preparation of sample is shorter and simpler than that for the radiocarbon analysis. 50 ml of water is necessary per analysis. The water samples are collected in glass bottles and sealed to avoid the evaporation and contact with atmospheric moisture.

The methane is obtained by chemical reaction of water with aluminium carbide:

$$Al_4C_3 + 12\,H_2O \rightleftharpoons 3\,CH_4 + 4\,Al(OH)_3 \qquad (3)$$

$$Al_4C_3 + 8\,H_2O \rightleftharpoons 3\,CH_4 + 4\,AlOOH \qquad (4)$$

$$Al_4C_3 + 6\,H_2O \rightleftharpoons 3\,CH_4 + 2\,Al_2O_3 \qquad (5)$$

The reaction follows mainly equation(3), however, the gas yield shows that the other two reactions (4,5) also take place simultaneously (7). The chemical reaction is carried out in a 5.5 l cylindrical stainless steel tank. The water steam reacts with the aluminium carbide.

Aluminium carbide is outgassed by heating the reaction vessel at 400°C before each reaction. The methane is passed through a column for chemical purification. The column is filled with copper oxide and heated to 600°C, followed by sodium hydroxide on asbestos and magnesium perchlorate absorbers (fig. 4).

The activity of methane is measured in the proportional counter. The construction of the counter is different from the counter for radiocarbon measurement (8). It is a multiwire proportional counter having 6.1 l total volume. The central anode is surounded by a ring of 15 anti-coincidence anodes and cathodes made of thin wire (fig. 5). The electronic equipment is similar to previously described system for radiocarbon measurement.

Some results of ^{14}C and ^{3}H measurements in underground and surface water

Tritium activity in monthly precipitation has been continuously measured since the end of 1975. in our Laboratory. Some results are given in table 1.

TABLE 1

Year	Month	Precipitation mm	Tritium activity T U
1978	1	47.1	37.7 ± 1.4
"	2	42.5	70.6 ± 1.7
"	3	70.5	82.9 ± 1.7
"	4	48.8	99.2 ± 1.9
"	5	115.2	121.2 ± 2.0
"	6	60.8	94.4 ± 1.9
"	7	105.5	102.2 ± 1.9
"	8	76.0	86.6 ± 1.8
"	9	72.4	85.8 ± 1.9
"	10	50.7	36.8 ± 1.5
"	11	14.7	38.4 ± 1.5
"	12	51.5	31.5 ± 1.1

Year	Month	Precipitation mm	Tritium activity T U
1979	1	107.7	29.5 ± 1.5
"	2	21.8	32.5 ± 1.1
"	3	78.7	31.6 ± 1.0
"	4	50.7	32.2 ± 1.4

Systematic measurements over four years have shown that the tritium concentration in the precipitation has periodical changes during the year. Maximum tritium concentrations have been measured at the end of spring and at the beginning of summer (from 170-190 T U). Considerable lower tritium activities were found in winter months, sometimes below 20 T U (fig. 6).

Tritium concentration in surface water is fairly constant as shown by systematic tritium measurement in Sava river.

Tritium concentrations in water of the National Park of Plitvice Lakes and that of tritium concentrations in precipitation present a possibility to develop a model of a hydro-dynamic system. Preliminary measurements during 1977. (table 2) have shown that there is no change of tritium concentration in lake water, as opposed to the precipitation water, although the mean value of activity of precipitation water (82 T U) and that of lake water (81 T U) are almost identical in the same period.

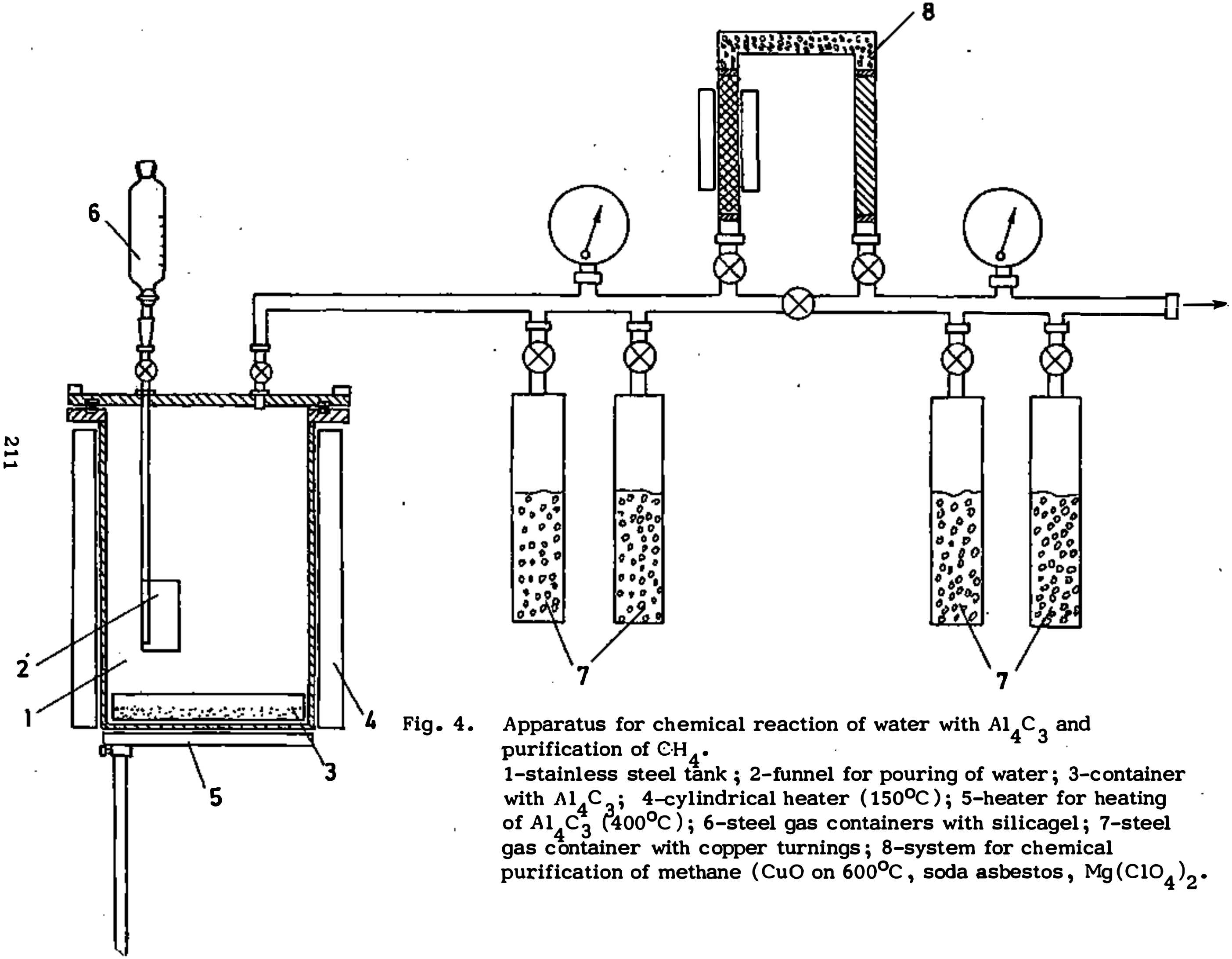

Fig. 4. Apparatus for chemical reaction of water with Al_4C_3 and purification of CH_4.
1-stainless steel tank ; 2-funnel for pouring of water ; 3-container with Al_4C_3 ; 4-cylindrical heater (150°C); 5-heater for heating of Al_4C_3 (400°C); 6-steel gas containers with silicagel; 7-steel gas container with copper turnings; 8-system for chemical purification of methane (CuO on 600°C, soda asbestos, $Mg(ClO_4)_2$.

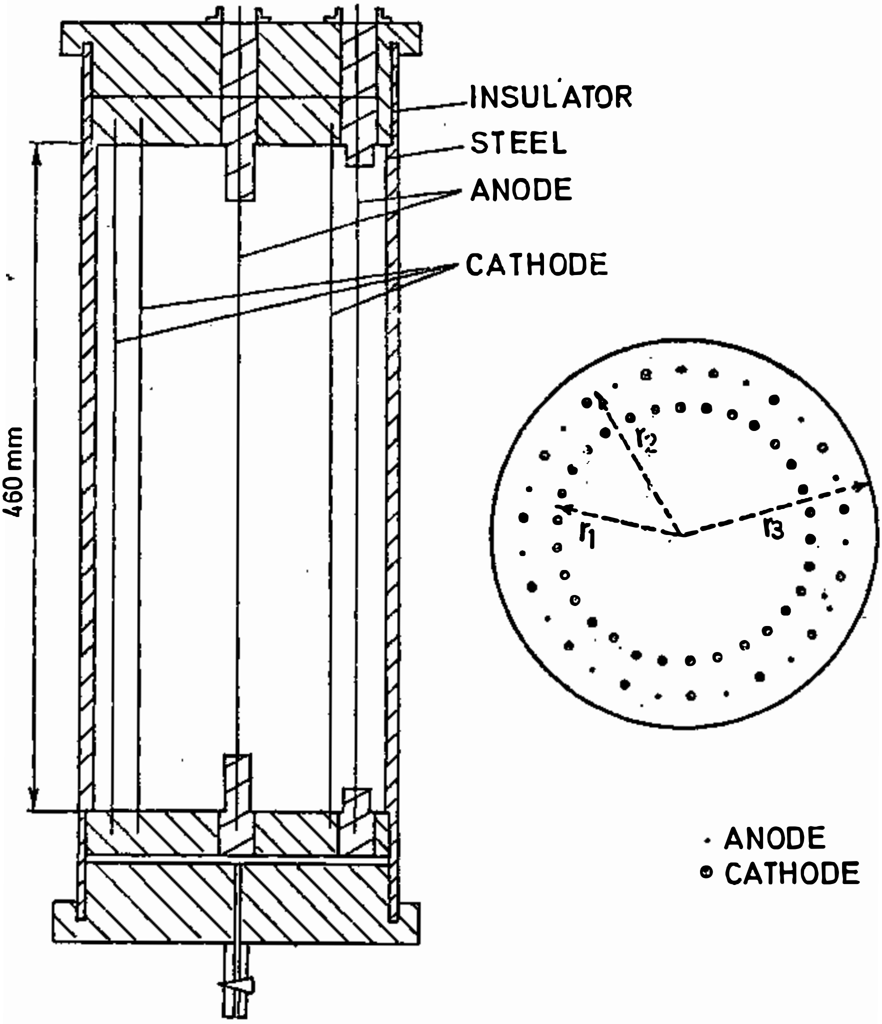

Fig. 5 Multiwire proportional counter.

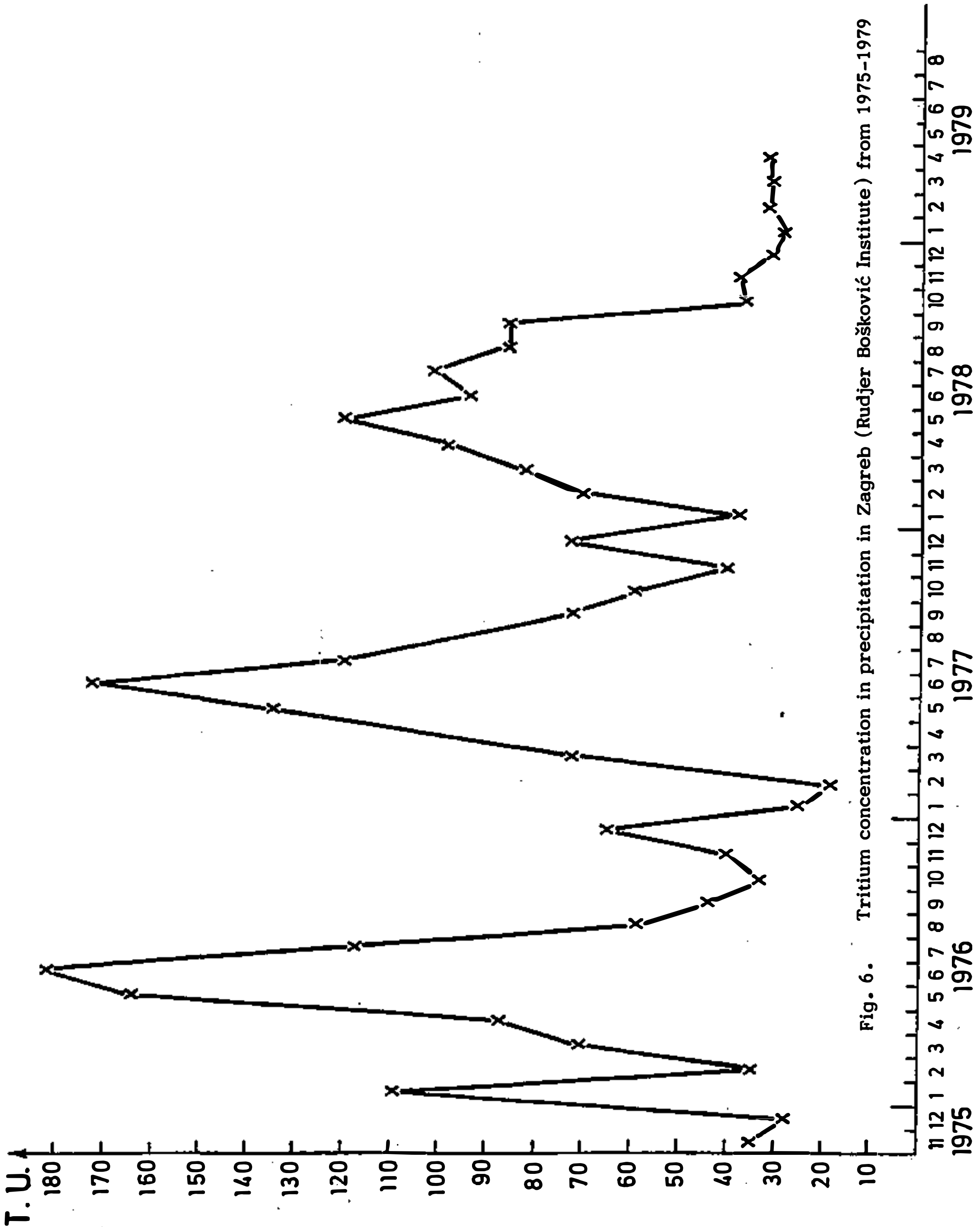

Fig. 6. Tritium concentration in precipitation in Zagreb (Rudjer Bošković Institute) from 1975-1979

TABLE 2

Sample		Tritium activity T U	
	2.10.1976.	12.5.1977.	6.9.1977.
Spring Kuselj	95.2 ±-2.0	93.8 ± 2.4	85.4 ± 1.9
Brook Plitvice	90.3 ± 2.0	82.5 ± 2.3	70.0 ± 1.8
Bijela rijeka, spring	72.0 ± 2.4	80.0 ± 2.3	65.7 ± 1.7
Bijela rijeka, stream	85.1 ± 1.8	88.0 ± 2.4	73.6 ± 1.8
Crna rijeka, spring	75.4 ± 1.7	70.6 ± 2.2	62.8 ± 1.7
Crna rijeka, stream	73.6 ± 2.4	71.2 ± 1.9	63.3 ± 1.8
Matica	84.2 ± 2.3	75.2 ± 2.3	67.0 ± 2.0
Brook Kavga	69.6 ± 2.3	71.5 ± 2.2	64.0 ± 1.7
Spring Pećina	77.7 ± 2.3	79.5 ± 1.9	67.7 ± 1.8
Brook Riječica	86.6 ± 2.5	86.1 ± 2.2	87.0 ± 1.9
Lake Galovac	79.5 ± 2.3	77.0 ± 3.0	70.4 ± 1.9
Lake Novakovića brod	74.5 ± 2.2	74.5 ± 2.2	74.4 ± 1.9

The systematic tritium measurements have been continued in the spring Crna rijeka and in spring Kuselj. Samples were taken once a month. Measurements which have been carried out up to now show that tritium concentrations in these springs are very constant. The difference in the tritium concentration between the two springs is about 20 T U (table 3).

TABLE 3

Date	Tritium activity T U Spring Crna rijeka	Spring Kuselj
23.6.1978.	55.7 ± 1.6	78.6 ± 1.8
15.7.1978.	59.6 ± 1.7	71.8 ± 1.8
20.8.1978.	56.7 ± 1.6	71.5 ± 1.8
23.9.1978.	54.3 ± 1.2	70.6 ± 1.8
24.10.1978.	51.9 ± 1.9	73.7 ± 1.3

The mean value of tritium concentration in precipitation is about 80 T U in the same time period. The data from tables 2 and 3 show that certain residence time and mixing of precipitate exists. The difference between activities of both springs could indicate a different residence time. It is necessary to continue with tritium measurements in Plitvice Lakes, National Park area. Then, in cooperation with hydrogeologists, it will be possible to obtain a complete interpretation of results.

Samples of groundwater from Libya have been measured as a part of a hydrogeological study carried out by Energoprojekt, Beograd. In addition to ^{3}H and ^{14}C, two stable isotopes, oxygen ^{18}O and deuterium ^{2}H, have been measured. Waters from thirty wells have been analysed. Some of the results are shown in table 4.

TABLE 4

Well	Depth m	Aquifer	^{14}C age yr	Tritium activity T U
Wadi Zamzam	172	Eocen	26 300 ± 900	3.0 ± 1.4
Wadi Zamzam	140	Eocen	14 200 ± 200	inactive
Wadi Zamzam	75	Eocen	24 300 ± 800	inactive
Abu Nujaym 1	450	Eocen	> 40 000	2.3 ± 0.9
Abu Nujaym 2		Eocen	> 40 000	3.0 ± 0.8
Socna 2	202	Socna	31 300 ± 1700	2.7 ± 1.4
Socna 4	193	Socna	34 100 ± 2240	inactive
Socna 11	150	Socna	> 40 000	inactive
Nesma 2	70	Tigrinna	11 200 ± 190	3. 8 ± 1.0
Khartum 6	180	Gharyan	19 000 ± 400	2.5 ± 1.6
Wadi Ghilan	460	Gharyan	22 800 ± 400	3.8 ± 1.1

The age has been calculated by using the initial concentration equal to 85% of the concentration of ^{14}C atoms in modern standard.
The youngest age of water sample is 10 000 years and the oldest age is more then 40 000 years. Tritium concentrations in a few samples indicate that some of the wells from the research area are influenced by the fresh precipitation. Tritium concentration in the majority of samples is below 10 T U indicating that the influence of precipitation on the groundwater is insignificant.

The results of radiocarbon and tritium analysis in combination with measurements of stable isotopes in groundwaters enable one to solve a many problems of interest to hydrologists and hydrogeologists:

The catchment area determination, the interaction between surface and groundwater, the season of catchment and the extent of an aquifer. From these facts the potentials of watersupplying can be determined. For the application and the proper interpretation of the isotopic results a cooperation of experts of different profiles as physicists, chemists, hydrologists and hydrogeologists is necessary.

Acknowledgement

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