Krypton-85 dating of shallow aquifer in Hebei Plain

ZHANG Xiang-yang[1, 2], CHEN Zong-yu[2], YANG Guo-min[1], TU Le-yi[1], HU Shui-ming[1*]

[1] University of Science and Technology of China, Hefei National Laboratory for Physical Sciences, Hefei 230026, China.
[2] Institute of Hydrogeology and Environmental Geology, CAGS, Shijiazhuang 050061, China.

Abstract: The inert gas radioactive isotope ^{85}Kr (with a half-life of 10.74 years), due to its stable physical and chemical properties, is an ideal tracer for shallow groundwater dating. In such a dating application, first the dissolved gas is extracted from groundwater in the field, then krypton is separated from the gas sample, and finally the isotopic abundance ^{85}Kr/Kr will be determined by an ATTA instrument. According to the atmospheric input curve of ^{85}Kr, the ^{85}Kr age of groundwater is determined. We conducted ^{85}Kr analysis in three wells in Zhengding County on the plains in front of the Taihang Mountains, and made a comparison with tritium (^{3}H) method.

Key words: Tracer analysis; Krypton-85; Tritium; Groundwater; Isotope dating

Introduction

Radioactive isotopes, known as the "geological clock", are widely used in the study of hydrological geology. The groundwater age usually refers to the average residence time of atmospheric precipitation from its infiltration underground to measurement site. Assuming that the aquifer system is closed, except the recharge and discharge of the groundwater, the system has no material exchange with the outside environment. The radioactive elements that enter into the aquifer will gradually decay according to its lifetime. By measuring the content of radioactive elements in the groundwater, and combining with its initial value and half-life, we can derive the groundwater age.

Since Libby W F *et al.* (1949) put forward the method of ^{14}C to measure carbon age, various radioactive isotopes have been applied to the dating of groundwater. Different radionuclides have different half-lives, therefore being applicable in different dating ranges.

The content of inert gas krypton in the atmosphere is 1.14 ppm (Verniani F, 1966). A radioactive isotope ^{85}Kr, is mainly produced in nuclear fission reaction and released into the atmosphere. The natural sources of ^{85}Kr, mainly the nuclear reactions between cosmic rays and stable krypton isotopes in the upper atmosphere, can be ignored compared with the amount of ^{85}Kr produced by human nuclear activities. At present, ^{85}Kr abundance in the atmosphere is about 2.5×10^{-11} (Kutschera W *et al.* 1994). Because the artificial nuclear activities are mainly distributed in the northern hemisphere, the ^{85}Kr distribution has regional difference in the world. Its concentration in the northern hemisphere is about 20% higher than that in the southern hemisphere, while being close in the same latitude. ^{85}Kr has a half-life of 10.74 years (Singh B and CHEN J, 2014), and is applicable to groundwater dating from 2 to 50 years.

In this study, we extracted the dissolved gas from the groundwater in the piedmont region of Hebei Plain, separated and purified krypton in the laboratory, and used Atom Trap Trace Analysis (ATTA) to measure the abundance of ^{85}Kr. The apparent age of ^{85}Kr is compared with the dating data which was derived using methods of tritium, ^{3}H-^{3}H and SF_6.

1 Working place

The research area, *i.e.*, Zhengding County, Hebei Province, is located in the piedmont region

*Corresponding author. E-mail: smhu@ustc.edu.cn

of Tailing Mountains. It's the groundwater recharge area for Hebei Plain. The terrain is flat and vast with an elevation of 60-90 m. The main climate type is the warm temperate zone continental monsoon climate. It's an arid and semi-arid area with a large temperature difference and unevenly distributed rainfall. Though the annual precipitation does not diverge on the geographical distribution, it has uneven intra-annual distribution, wide inter-annual variations. The characteristics of continued dry season and continued high-water season are not conducive to the formation and utilization of groundwater resources. The Hutuo River is the biggest river in the study zone with a large catchment area, and it has wide river bed and flood plain. Before 1959, water was flowing in the Hutuo River all the year round. Since the 1960s, the Huangbizhuang Reservoir and the Gangnan Reservoir in the upper reaches have stored water which is under artificial control. The Hutuo River is dry all the year round, and generally only in the flood season a small amount of water will pass through.

The groundwater in the study zone is the Quaternary unconsolidated rock pore water. The aquifers contain sandy pebble, sand gravel and coarse sand in the upper Pleistocene-Holocene series and middle Pleistocene series with abundant water and good water quality.

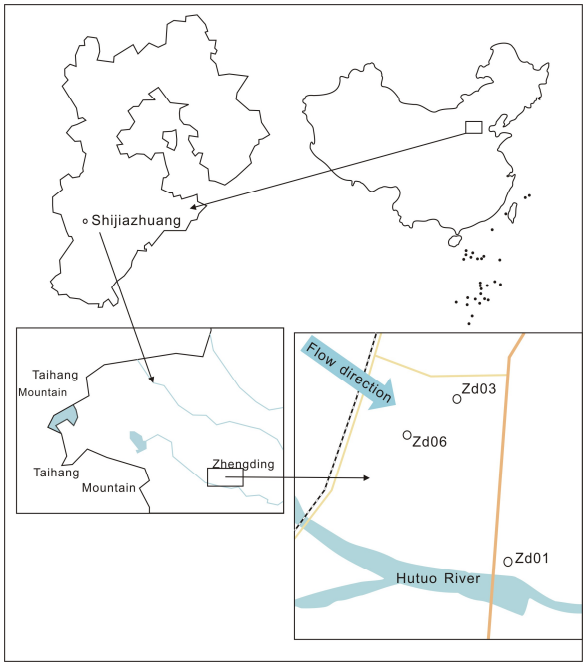

Fig. 1 The study area

The sampling site is located in Zhengding with ZD01 on the north bank of the Hutuo River, ZD02 and ZD03 located in Zhengding County. The well is 60-100 m in depth, and the depth to water level is 30 m.

2 Method

2.1 Extraction of dissolved gas

The sample gas was obtained by using the vacuum spray method to extract the dissolved gas from groundwater. The whole system consists of a vacuum cavity waterway and gas paths of gas collection, as shown in Fig. 2. The groundwater sample, after filtering and a booster pumping, is sent into a vacuum chamber made of organic glass for degassing. Atomization effect greatly increases the gas - liquid phase contact area. The sample gas dissolved in water rapidly emerges, and then is periodically compressed by the compressor in the gas paths into the sampling cylinder. Liquid water is continuously discharged out of the system by the magnetic drive pump at the bottom. In the process of sampling, the water temperature, water pressure, flow velocity and the pressure of dissolved gas were recorded in real time by water temperature meter, water pressure gauge, flow meter and barometer, respectively. The ultimate vacuum of the diaphragm pump used in the system is 100 Pa, which guarantees the vacuum degree of the gas pipeline before sampling. The backing pressure of the compressor can reach 80 mBar, and its maximum compressible gas pressure is 4 Bar. The volume of the sampling tank is 4 L with a maximum pressure of 4 Bar.

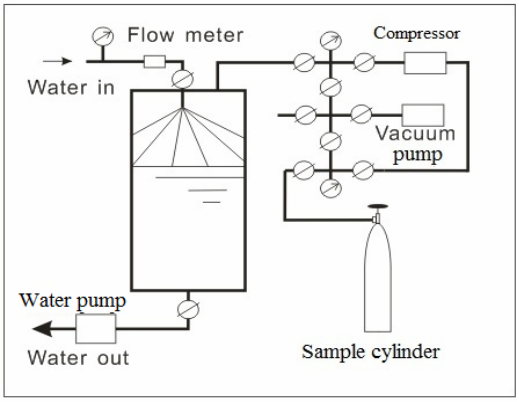

Fig. 2 Vacuum atomization sampling device

Samples under high pressure condition, after

atomization nozzle goes into the vacuum chamber and atomizes rapidly. According to Henry's Law, the solubility of gas in water shall be directly proportional with the equilibrium partial pressure of gas under the condition of constant pressure and temperature. When the sample water comes into a vacuum environment with extremely low gas pressure, the dissolved gas in water will quickly precipitate into the vacuum chamber to reach rebalance of gas solubility. At the beginning of the experiment, the organic glass cavity is filled with raw water and then initial vacuum is prepared by sucking water drainage pump. Raw water with certain pressure continues into the vacuum chamber for degassing through atomizing the nozzle. When gas reaches a certain amount, the water levels begin to decline. When the vacuum chamber is filled with gas, the gas sample is collected into the tank with the compression pump.

Table 1 The sampling record of dissolved gas

Sample ID	Well depth (m)	Sampling time	Sample volume (L)
ZD01	60	2014-4-23	7
ZD02	100	2014-5-15	5.4
ZD03	100	2014-4-15	5.5

2.2 The purification of Krypton

To meet the needs of measurement, krypton gas should be purified from the collected dissolved gas. The separation process (Fig. 3) includes two steps: Cryogenic distillation and gas chromatographic separation. (1) Cryogenic distillation. Gas samples, after filtering with a 5A molecular sieve to remove water and carbon dioxide, are frozen into the cold trap 1 at liquid nitrogen bath (-196 ℃) with activated carbon. The gas is drawn out from the cold trap by a vacuum pump at a flow rate of 0.2 L/min. Stop extraction when the sample is about 0.2 L left. The rest will be mainly nitrogen, oxygen and argon gas. Then krypton is rich in residual gas. The high temperature Titanium furnace (1 000 ℃) removes most of the active gas in the residual gas which has a volume of 10 ml and is gathered in the cold trap 2; (2) gas chromatographic separation. Gas in cold trap 2 will be baked out at 150 ℃, and then will be taken by helium carrier gas into the gas chromatograph for the eventual separation and collection of Kr. The carrier gas has a flow rate at 45 ml/min. The chromatographic column is 6 mm in diameter and 2 m long, with 5A molecular sieve. It can effectively separate Ar, N_2, and Kr at 25 ℃. A thermal conductivity detector (TCD) is used to monitor the peak time of each gas component. After collecting krypton peak, repeat the chromatography process to get pure krypton gas.

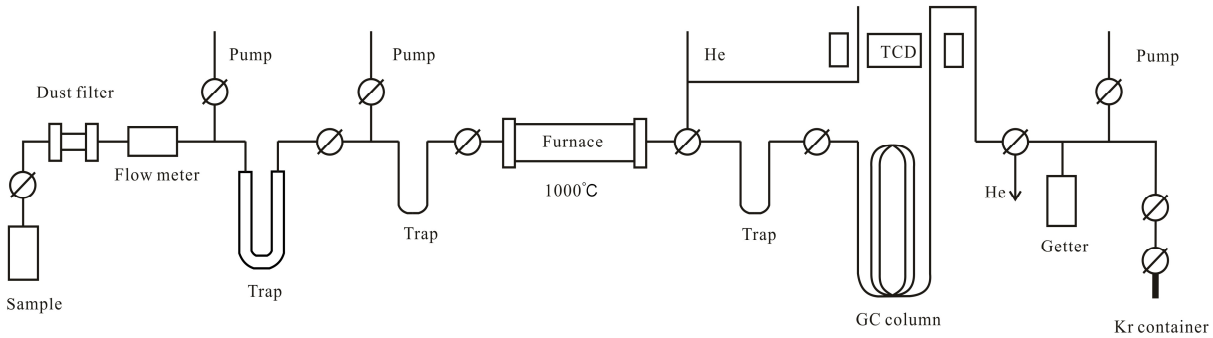

Fig. 3 Schematic diagram of Kr gas purification system

2.3 ^{85}Kr measurement

The measurement of ^{85}Kr is conducted with the ATTA set up in USTC.

ATTA method is a technology based on the interaction of laser and the atom. By controlling the laser frequency, target isotope atoms are trapped in a magneto-optical trap (MOT), and each single atom will be counted. Laser has multiple interactions only with atoms that match its frequency. ATTA has extremely high selectivity, and will never capture other atoms or molecules by mistake. Laser wavelength in the experiment is 811.5 nm on resonance with the $5s[3/2]_2 \rightarrow 5p[5/2]_3$ transition of Kr. Krypton after liquid nitrogen precooling, via radio frequency discharge, is

excited to the metastable state $5s[3/2]_2$ (about 40 s of natural life). After two-dimensional laser beam transverse cooling and weak focusing, a collimated high brightness metastable Kr atomic beam is formed. The atomic beam after Zeeman deceleration coil was slowed down to 30 m/s or so, and finally captured in the MOT. For isotope ^{85}Kr, due to its low isotopic abundance, MOT can only capture a few atoms per second. Each trapped atom scatters about 10^7 photons per second. A sensitive EMCCD camera is used to image the fluorescence signal of a single atom. In this way, single atom counting is realized.

3 Results

3.1 ^{85}Kr

Samples from three well points were analysed and the results are shown in Table 2.

Table 2 Analysis results of samples ^{85}Kr

Sample ID	Kr gas (μL)	^{85}Kr activity (dpm/cc)	^{81}Kr (pMKr)	^{85}Kr age (year)
ZD01	12.9	23.6±1.1	101±4	16.6±0.5
ZD03	15.4	12.6±1.2	105±6	23.1±1.1
ZD06	13.4	16.4±0.9	108±6	20.4±0.6

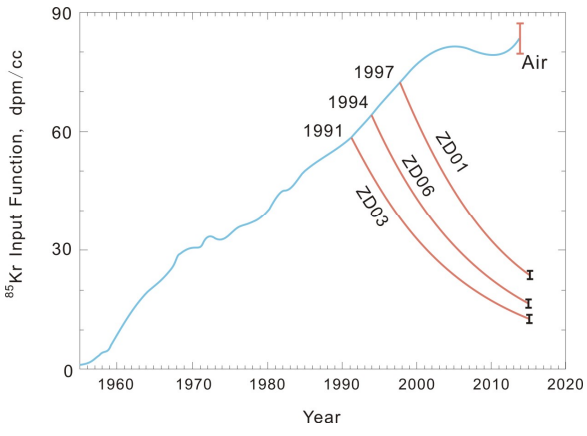

Fig. 4 ^{85}Kr age of samples

The ^{85}Kr atmospheric input curve is derived according to the ^{85}Kr/Kr data in Hebei air and the historical data of Europe in the literature (Corcho Alvarado J A *et al.* 2007; Bollhöfer A *et al.* 2014; Ross O, 2010; Różański K, 1979; Ekwurzel B *et al.* 1994; Weiss W *et al.* 1989; Kinzelbach W, 2010). According to ^{85}Kr concentration and half-life of the sample, we can backstep the intersection point of the decay curve and the atmospheric input curve, and get the supply year of ^{85}Kr, as shown in Fig. 4. Three samples have an apparent ^{85}Kr age between 17-24 years.

Table 3 Analysis results of samples tritium

Sample ID	^{3}H (TU)	EPM age (a)	Determined age (a)
ZD01	9.5±1.0	6-10, 22-32	22-32
ZD03	11.8±1.2	1-6, 32-35	32-35
ZD06	14.2±1.5	2, 33-40	33-40

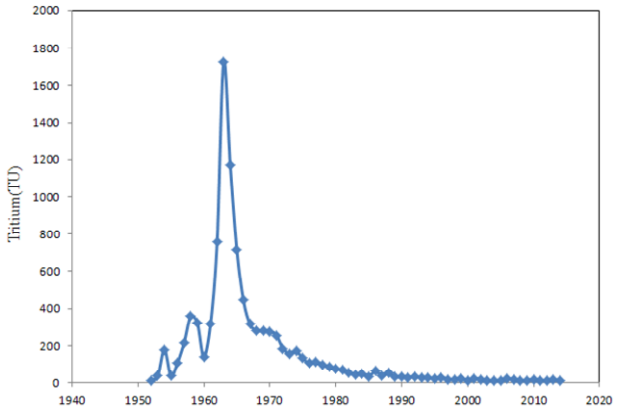

Fig. 5 Tritium input concentration in precipitation in Shijiazhuang

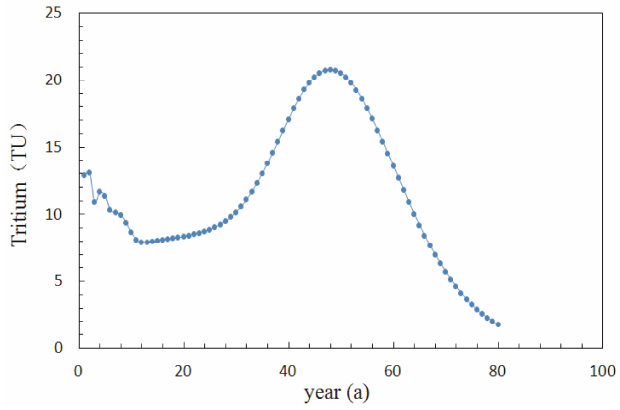

Fig. 6 Tritium output concentration curve from the EPM model (2014)

3.2 Tritium

Tritium (^{3}H) is a radioactive isotope of hydrogen with a half-life of 12.32 years. Because it is a part of the water molecule, tritium is considered to be an ideal tracer for dating groundwater. The tritium age was calculated by

using lumped parameter models (Maloszewski P and Zuber A, 1996). The determination of tritium input function plays a pivotal role in interpreting the tritium data. The tritium input data in Shijiazhuang station is available in the global network of isotopes in precipitation (GNIP) of IAEA. The tritium input and output concentration in precipitation are shown in Fig. 5 and Fig. 6. According exponential piston flow model (EPM), the ages of the groundwater are shown in Table 3.

4 Conclusions and discussions

The analysis according to ^{85}Kr and tritiumdata shows that the groundwater under three well points are modern water. It suggests that using ^{85}Kr for dating is basically reliable though the ages of ^{85}Kr are about 10 years younger than those of tritium. Because the aquifer is shallow, the sand layer develops, and the permeability is good, there might be atmospheric infiltration in the aquifer, leading to a higher ^{85}Kr/Kr abundance in the groundwater and a low apparent age.

Acknowledgements

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