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Purification of hydrogen isotopes using palladium molecular sieve

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Abstract

The purification of hydrogen isotopes is often carried out in tritium technology. A lot of methods are in use now. Palladium molecular sieve has some unique advantages. It was used to purify hydrogen isotopes with impurities such as helium, air and carbon dioxide in this experiment. There are a lot of factors that affect the purification effect of palladium molecular sieve. Working temperature and filling rate are the most important two factors. A series of one-cycle purification experiments were carried out to select the appropriate working temperature and filling rate. The selected filling rate of raw gas was 30 ml/min, and the absorption and desorption temperature were 223 and 473 K, respectively. Hydrogen isotopes with impurities were purified in only one cycle and the purified gas was greater than 99.0% pure. In addition, the purification experiment showed that resistance to poisoning of palladium molecular sieve was excellent.

1. Introduction

The purification of hydrogen isotopes is often carried out in tritium technology [1–4]. Palladium–silver diffusion device is the most commonly used now. This device can purify large amount of raw gas and the purity achieved is very high. However, the cost and working temperature are high. So it is necessary to search for a material which can purify hydrogen isotopes with impurities such as He, O_2, N_2 and CO_2 and which purification efficiency is high. The material must be unlikely to be poisoned easily and the price is not costly. A kind of purification technology by palladium molecular sieve was developed at the end of 1980s. The device developed by this technology was compact and the cost was low. The working temperature was lower (the maximal working temperature is about 473 K), and so the environmental pollution by diffused tritium is lower too [5–8]. The basic principle of purification is as follows: hydrogen isotopes are absorbed in palladium at a lower temperature (such as 223 K), and impurities such as He, O_2, N_2 and CO_2 cannot be absorbed. These impurities can be removed by pumping. The absorbed gas can be desorbed almost completely at 473 K and the purity of desorbed hydrogen isotopes is higher than 99.0%.

2. Experimental

A purification system was designed and developed (Fig. 1). In the system, the purification utensil was filled with 50 ml palladium molecular sieve with grain size 40–60 screen mesh and palladium content 40% (wt). The process of purification was as follows: after measuring, the mixture from raw gas tank flowed into the purification utensil which was dipped in a kind of ice–salt solution at a certain rate and the gases which cannot be absorbed were pumped into the remnant gas tank at the same time. The process did not terminate until the purification utensil could not absorb gases any more. Then the ice–salt solution was removed and the purification utensil was heated to 473 K to desorb the gases. The desorbed gases amount were measured by PVT method. Purified gas and remnant gas were analyzed by mass spectrograph.

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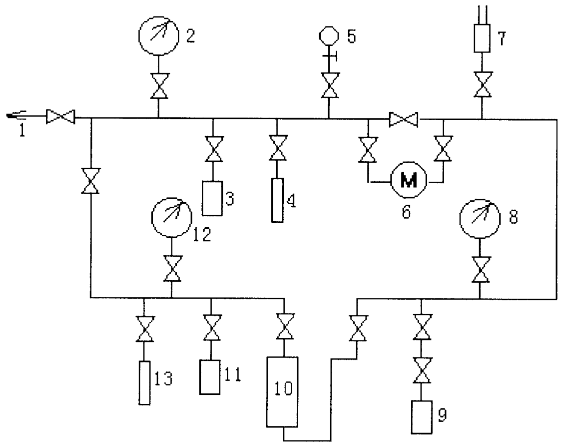

Fig. 1. Schematic diagram of hydrogen isotopes purification system. (1) To vacuum system, (2, 12) pressure meter, (3) remnant gas tank, (4, 13) measuring tank, (5) sampling bottle, (6) circulating pump, (7) vacuum sensor, (8) vacuum meter, (9) uranium bed, (10) purification utensil, (11) raw gas tank.

3. Results and discussion

3.1. Selection of purification condition

There are a lot of factors that affect the purification effect of palladium molecular sieve. Working temperature and filling rate are the most important two factors. Comparison experiments were carried out for the selection of appropriate working temperature and filling rate. The results are showed in Tables 1 and 2.

Table 1 shows the one-cycle purification results at different temperatures for the same filling rate condition. The filling rate was 30 ml/min and the absorption temperatures were 223 and 253 K. The composition of raw gas was 90.42% hydrogen isotopes and 9.58% helium. When the absorption temperature was 253 K, the content of hydrogen isotopes in the remnant gas was 13.8%. So it was too high and not appropriate. When the absorption temperature was 223 K, the purity of purified gas and the recovery ratio were high, and the content of hydrogen isotopes in the remnant gas was lower. If the absorption temperature was further reduced, the content of hydrogen isotopes in remnant gas would reduce too. However, a lower temperature would affect the hydrogen isotopes absorption properties and there was some difficulty to lower temperature. The results were satisfactory when the absorption temperature was 223 K, so it is not necessary to further lower the absorption temperature.

Table 2 shows the one-cycle purification results at different filling rates for the same temperature. The absorption temperature was 223 K and the desorption temperature was 473 K. The filling rates were 30, 44 and 84 ml/min. From Table 2, we can conclude that the quicker the filling rate, the higher the content of hydrogen isotopes in the remnant gas, but the filling rate did not affect the purity of purified gas. When the filling rate was 30 ml/min, the purity of purified gas and the recovery ratio were high, and that the content of hydrogen isotopes in the remnant gas was lower. Based on the above results, the selected purification condition was as follows:

1. The absorption and desorption temperature of purification utensil were 223 and 473 K, respectively.
2. The filling rate was 30 ml/min.

Table 1
Purification effect at different absorption temperatures

Absorption temp. (K)	Composition of purified gas		Composition of remnant gas		Recovery ratio (%)
	C_{He} (%)	C_H (%)	C_{He} (%)	C_H (%)	
223	–	>99.99	98.0	2.0	99.78
253	–	>99.99	86.5	13.8	98.35

Note: '–' means not detected.

Table 2
Purification effect of different filling rate, with absorption temperature 223 K

Filling rate (ml/min)	Composition of purified gas		Composition of remnant gas		Recovery ratio (%)
	C_{He} (%)	C_H (%)	C_{He} (%)	C_H (%)	
84	–	>99.99	89.81	10.19	98.74
44	–	>99.99	96.12	3.88	99.60
30	–	>99.99	98.0	2.0	99.78

3.2. Purification of hydrogen isotopes with impurities such as He, air and CO_2

Purification of hydrogen isotopes with impurities such as He, air and CO_2 was carried out at the above-mentioned condition. The results are showed in Tables 3–5.

Table 3 showed the one-cycle purification results of hydrogen isotopes with impurity He. The contents of He were 9.58%, 48.69% and 89.33%. The palladium molecular sieve can remove He from hydrogen effectively and the higher the content of He, the better purification.

Table 4 shows the one-cycle purification results of hydrogen isotopes with impurity air. The contents of air were 9.39% and 50.01%. The purity of purified gas was very high, but the content of hydrogen isotopes in remnant gas was relatively high and the recovery ratio was relatively low. This was likely caused by the absorption of air on the surface of the palladium molecular sieve. The absorption of air increased the difficulty of dissolving of hydrogen isotopes in palladium. The content of hydrogen isotopes in remnant gas could be reduced by multi-cycle purification.

Table 5 shows the one-cycle purification results of hydrogen isotopes with impurity CO_2. The contents of CO_2 were 14.3% and 43.6%, respectively. The palladium molecular sieve can remove CO_2 from hydrogen isotopes effectively.

3.3. Verification of poisoning resistance of palladium molecular sieve

Before the purification experiment, the quantity of dissolved hydrogen in the purification utensil was 1423.9 ml. The quantity was 1415.8 ml after the purification of hydrogen isotopes with impurities such as He, air and CO_2. The quantities were almost the same, and it showed that the resistance to poisoning of palladium molecular sieve was excellent.

4. Conclusions

Palladium molecular sieve can purify hydrogen isotopes with impurities such as He, air and CO_2 effectively in one cycle. The purified gas was greater than 99.0% pure. In order to purify hydrogen isotopes effectively, appropriate working temperature and filling rate must be selected. In this experiment, the filling rate of raw gas was 30 ml/min, and the absorption and desorption temperature were 223 and 473 K, respectively.

Table 3
Purification of hydrogen isotopes with impurity He

No.	Composition of raw gas		Composition of purified gas		Composition of remnant gas		Recovery ratio (%)
	C_{He} (%)	C_H (%)	C_{He} (%)	C_H (%)	C_{He} (%)	C_H (%)	
1	9.58	90.42	–	>99.99	98.0	2.0	99.78
2	48.69	51.31	–	>99.99	99.44	0.56	99.94
3	89.33	10.67	–	>99.99	>99.99	–	99.99

Table 4
Purification of hydrogen isotopes with impurity air

No.	Composition of raw gas		Composition of purified gas		Composition of remnant gas		Recovery ratio (%)
	C_{air} (%)	C_H (%)	C_{air} (%)	C_H (%)	C_{air} (%)	C_H	
1	9.39	90.61	0.24	99.76	71.99	18.01	96.50
2	50.01	49.99	0.05	99.95	97.65	2.84	97.09

Table 5
Purification of hydrogen isotopes with impurity CO_2

No.	Composition of raw gas		Composition of purified gas		Composition of remnant gas		Recovery ratio (%)
	C_{CO_2} (%)	C_H (%)	C_{CO_2} (%)	C_H (%)	C_{CO_2} (%)	C_H (%)	
1	14.3	85.7	0.28	99.72	98.44	1.56	99.15
2	43.6	56.4	0.86	99.14	99.13	0.87	99.03

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