Methodological Study on Measurement of Hydrogen Abundance in Hydrogen Isotopes System by Low Resolution Mass Spectrometry

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Abstract: China's rapid economic growth has resulted in significant environmental side effects. Therefore, China has been interested in reducing her dependence on foreign oil and gas by developing technologies needed for hydrogen, in addition to her increasing energy mix of nuclear and renewable energy form, such as solar and wind power. There are three isotopes of hydrogen, i.e. protium (P or H), deuterium (D), and tritium (T). Both deuterium and tritium are important materials in nuclear fuel cycle industry. Tritium is one of the critical radioactive nuclides. Planning for and implementing contamination control as a part of normal operation and maintenance activities is an important function in any hydrogen facility, especially tritium facility. The development of hydrogen isotopes analysis is the key issues in this area. Mass spectrometry (MS) with medium (about 600) and high resolution (> 1,400) is commercially available; however, the routine analysis of hydrogen isotopes is done with low-resolution MS (< 200) in China. This paper summarizes the progress of MS measurement technology for hydrogen isotope abundance in China, focusing on our lab's research program and technical status. An analyzing method has been introduced for accurate measurement of tritium abundance in the H–D–T system by low resolution MAT-253 MS. The quotient of compression ratio coefficient is determined by building up equipment for laboratory-scale preparation of secondary standard gases and by considering the difference in sensitivity between hydrogen isotopes. The results show that the measured value is reproducible within the relative error range of 0.8% for gas samples of different tritium abundance.

Key words: Hydrogen Isotopes, Tritium Abundance, Low Resolution Mass Spectrometry, Compression Ratio Coefficient

China's rapid economic growth has resulted in significant environmental side effects. For instance, industrial emissions from factories have caused serious acid rain problems. Moreover, a significant increase in car sale has led to a corresponding rise in carbon emissions from the country's transportation sector, contributing to China's air pollution problems. Therefore, China has been keenly interested not only in reducing her dependence on hydrocarbon fuel by developing technologies needed for hydrogen and fuel cells but also in combining nuclear and renewable energy (solar and wind power). Especially, technologies needed for hydrogen are key elements in a portfolio of advanced energy technologies that China National Development and Reform Commission is developing to address energy challenges today and in the future. There are three isotopes of hydrogen, i.e. protium (P or H), deuterium (D), and tritium (T). Both deuterium and tritium are important materials in nuclear fuel cycle industry, as well. Tritium is one of the critical radioactive nuclides. Planning for and implementing contamination control as a part of normal operation and maintenance activities is an important function in any hydrogen facility, especially tritium facility.

The use of hydrogen as an energy carrier has the potential to reduce the dependence on petroleum and the decrease in pollution and greenhouse gas emissions. Therefore, technologies needed for hydrogen are in active development and in validation, in addition to complementary near-term energy efficiency and renewable energy solutions, such as ethanol and hybrid electric vehicles. Many hydrogen programs make significant progress toward achieving the goal of reducing the cost and increasing the performance by research and development, as well as by validation of hydrogen production, storage, and etc. The programs work in partnership with diverse organizations, including automotive and power equipment manufacturers, energy and chemical companies, electric and natural gas utilities, code and standards development organizations, federal and state agencies, universities, national laboratories, and other national and international stakeholders. The development of hydrogen isotopes analysis is the key issues in these areas.[1]

There are two kinds of laboratory measurement of hydrogen, radioactivity[2,3] and non-radioactivity measurement.[4–6] Radioactivity measurement is suitable for laboratory analysis on samples with tritium. There are many methods for the non-radioactivity measurement, i,e., gas chromatograph (GC), mass spectrometry (MS), gas chromatograph-mass spectrometry (GC-MS), spectroscopy, and etc. GC needs a cryogenic separation column because

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the difference in sorption rate among hydrogen isotopes becomes larger at lower temperature. However, the cryogenic GC has the disadvantage of long retention time, typically tens of minutes. GC-MS has the similar disadvantage. MS has been accepted as a rapid, accurate technique for hydrogen analysis. In addition to the excellent sensitivity, MS allows abundance measurements.[7,8]

Fully-automated analysis of hydrogen isotopes system has been a target for several decades. β radiations from tritium catalyse the exchange reactions. Mixtures of H_2, D_2, and T_2 in the gas phase will not remain isotopicaly pure for a long time.[9] The mixed molecules (HT, DT, and HD) are obtained rapidly in less than 24 h.[10] Previously, without adequate resolving power, many mass spectrometrists have relied upon equilibrium constants and assumed the establishment of equilibrium, which, on many occasions, has led to serious errors. In 1954, the American chemist B.B. McInteer, Los Alamos National Laboratory of the University of California Los Angeles has reported the analysis of H/D/T gas mixtures with low resolution MS. In the general middle range of ternary concentrations, the average accuracy was better than 0.4%. In the seventies, K W Foster, P. Chastagner, W. A. Youg, and T. K. Mehrhoff have optimized the method of analysis of H/D/T gas mixtures with low resolution MS. In the lower range of ternary concentrations (5%), the average accuracy within 2% could be made by using accurately mixed standards. In 1982, the American chemist P. Chastagner at the Savannah River Laboratory of the South Carolina has established the design of analysis of H/D/T gas mixtures with high resolution MS. The average accuracy within 0.5% could be made by resolving peaks of D^+ and H_2^+, HD^+ and $^3He^+$, D_2^+ and HT^+ using high resolution MS. Very few references have been published lately.

A routine analysis of H/D/T gas mixtures in China has been done with low resolution MS. High resolution MS must be introduced from developed countries, and are laid an embargo on commerce with China. In 1985, MS analysis of high abundance tritium isotope by a modified type ZhT-1301 MS has been described by Liu Qi (Beijing Research Institute of Uranium Geology) and Deng Zhong-guo (China Institute of Atomic Energy).[11] The measured accuracy was 0.04% with the abundance over 99%. In the nineties, Luo Xue-jian, Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, has established the method of analysis of H/D/T gas mixtures with high (>3000) resolution MS (MAT-271) with less than 0.5% accuracy. In 2000's, Shi Lei,[12–14] Huang Gang,[15] and Zhang Hai-lu[16] have improved on analysis of H/D/T gas mixtures with low resolution MS. Especially, Shi Lei modified an analyzing method for accurate measurements of deuterium abundance in the hydrogen-deuterium system by low (about 25) resolution MAT-253. Their results showed that, for gas samples of different deuterium abundance, the measured value was believable with the relative error of 0.5%. In addition, Shi Lei[12,13,17,18] carried out a series of studies, including methodological check computations and modifications on the abundance measurement of hydrogen

isotopes system, key techniques on gas preparation of hydrogen isotopes, and contrast analyses of abundance measurement Their results was assessed to be satisfactory.

Nowadays, we need to analyze a wide range of mixtures of the hydrogen and helium isotopes. All of the ions shown in Table 1 are present in MS. The monatomic hydrogen ions are found in fixed ratios to their parent diatomic ions. They are subtracted from the MS peaks without any difficulty. The helium must be either separated from the hydrogen or measured separately. Moreover, ^3He must be resolved from HD, while ^4He from HT and D_2. The HT-D_2 doublet can be either resolved or measured, whereas the HT and D_2 values can be calculated from the HT, DTl and T_2 values using the equilibrium constants. In the latter case, the sample must be at the equilibrium state.

A theoretical study of the MS analysis of hydrogen isotopes shows that mass discrimination and low ion abundance in ion sources are the principal factors that limit accuracy. An Einzel ion source with a short focal length and high brightness avoids these limitations. Suitable analyzers and accessory equipment are available. A high resolution mass spectrometry can analyze mixtures of the hydrogen isotopes system accurately within 0.5% with ordinary operating techniques, whereas a

Table 1. Important Ions in the Mass 2~6 Range.

Species	m/z	Resolution[a] Required
D^+	2.0140	
		1220
H_2^+	2.01565	
		2.5
$^3He^+$	3.01603	
		155000
T^+	3.01605	
		520
HD^+	3.021825	
		1830
H_3^+	3.023475	
		3.5
$^4He^+$	4.00260	
		160
HT^+	4.023875	
		980
D_2^+	4.028	
		4.5
DT^+	5.03005	
		5.5
T_2^+	6.032	
		610
D_3^+	6.0420	

[a]Resolution : 10% valley definition

low resolution MS can analyze mixtures of the hydrogen isotopes accurately within 2% with accurately mixed standards.

1. Modified low-resolution MS analysis of hydrogen isotopes system with calibration coefficient

In theory, it is possible that an analysis of the six species (H_2, D_2, T_2, HD, HT, and DT) of hydrogen isotopes system with low-resolution MS, since six individual mass peaks can be measured; i.e., six equations with six unknowns, as written below:

$$I_1 = 2a_{11}I(H^+_2)+a_{12}I(HD^+)+a_{13}I(HT^+) \quad (1)$$

$$I_2 = I(H^+_2)+a_{21}I(HD^+)+2a_{22}I(D^+_2)+a_{23}I(DT^+) \quad (2)$$

$$I_3 = I(HD^+)+a_{31}I(HT^+)+a_{32}I(DT^+)+2a_{33}I(T^+_2) \quad (3)$$

$$I_4 = I(D^+_2)+I(HT^+) \quad (4)$$

$$I_5 = I(DT^+) \quad (5)$$

$$I_6 = I(DT^+_2) \quad (6)$$

where I_1, I_2,…is the peak height of the various mass numbers measured, respectively, and a_{11},a_{12},…is the ratio of the following monatomic ions contribution to the peak height of the parent molecule, respectively, which can be measured or computed using the Frank-Condon principle[10] (i.e. a_{11} is the ratio of the H^+ on I_1, a_{32} is the ratio of the D^+ on I_3, etc.). The following reactions can be used:

$$D_2+T_2 = 2DT, \ K_{DT} = \frac{I(DT)^2}{I(D_2)I(T_2)} = 3.82$$

(at room temperature).

The D_2 component can be computed from the T_2 and DT intensities, HT from the peaks at m/z 4, HD from Equation (3), and D_2 from Equation (2). Results are summarized in the following equations:

$$I(D^+_2) = \frac{(I_5)^2}{3.82I_6} \quad (7)$$

$$I(HT^+) = I_4-I(D^+_2) = I_4-\frac{(I_5)^2}{3.82I_6} \quad (8)$$

$$I(HD^+) = I_3-a_{31}I(HT^+)-a_{32}I(DT^+)-2a_{33}I(T^+_2) \quad (9)$$

$$I(H^+_2) = I_2-a_{21}I(HD^+)-a_{22}I(D^+_2)-2a_{23}I(DT^+) \quad (10)$$

where a_{11}, a_{22}, … are the coefficients of the various species on the various mass numbers. The coefficients for this analysis are the ratios of the monatomic contribution toward any one mass unit to the peak height of the parent molecule. The ratio of the monatomic contribution toward any one mass unit can be written as follows:

$a_{11} = (0.323\pm0.001)\%$, $a_{22} = (0.273\pm0.004)\%$, $a_{33} = (0.220\pm0.003)\%$, $a_{12} = a_{21} = (0.297\pm0.004)\%$, $a_{13} = a_{31} = (0.267\pm0.003)\%$, $a_{23} = a_{32} = (0.245\pm0.004)\%$.

Abundance computation equations of hydrogen isotopes system can be written as follows:

$$\phi(T)=\frac{I(T^+_2)+0.5I(DT^+)+0.5I(HT^+)}{I(H^+_2)+I(D^+_2)+I(T^+_2)+I(HD^+)+I(HT^+)+I(DT^+)} \quad (11)$$

$$\phi(D)=\frac{I(D^+_2)+0.5I(HD^+)+0.5I(DT^+)}{I(H^+_2)+I(D^+_2)+I(T^+_2)+I(HD^+)+I(HT^+)+I(DT^+)}$$

$$\phi(H) = 1-\phi(D)-\phi(T)$$

where $\phi(H)$, $\phi(D)$, and $\phi(T)$ is the abundance of protium, deuterium, and tritium, respectively. Providing the mass discrimination is not too severe and high-purity calibration gases are available, mass discrimination can be managed using normal calibration procedures.

Improvements have been made by Shi Lei,[12,13,16,17] Huang Gang,[14] and Zhang Hai-lu[15] using the compression ratio coefficient in low-resolution MS analysis of hydrogen isotope system. The following is the equations of abundance measurements in hydrogen isotopes system:

$$\varphi(T) =$$

$$\frac{\dfrac{e^{k/6}I(T^+_2)}{\sqrt{6}}+0.5\dfrac{e^{k/5}I(DT^+)}{\sqrt{5}}+0.5\dfrac{e^{k/4}I(HT^+)}{\sqrt{4}}}{\dfrac{e^{k/2}I(H^+_2)}{\sqrt{2}}+\dfrac{e^{k/4}I(D^+_2)}{\sqrt{4}}+\dfrac{e^{k/6}I(T^+_2)}{\sqrt{6}}+\dfrac{e^{k/4}I(HD^+)}{\sqrt{4}}+\dfrac{e^{k/4}I(HT^+)}{\sqrt{4}}+\dfrac{e^{k/5}I(DT^+)}{\sqrt{5}}}$$

$$\varphi(D) =$$

$$\frac{\dfrac{e^{k/4}I(D^+_2)}{\sqrt{4}}+0.5\dfrac{e^{k/4}I(HD^+)}{\sqrt{4}}+0.5\dfrac{e^{k/5}I(DT^+)}{\sqrt{5}}}{\dfrac{e^{k/2}I(H^+_2)}{\sqrt{2}}+\dfrac{e^{k/4}I(D^+_2)}{\sqrt{4}}+\dfrac{e^{k/6}I(T^+_2)}{\sqrt{6}}+\dfrac{e^{k/4}I(HD^+)}{\sqrt{4}}+\dfrac{e^{k/4}I(HT^+)}{\sqrt{4}}+\dfrac{e^{k/5}I(DT^+)}{\sqrt{5}}}$$

$$\varphi(H) = 1-\varphi(D)-\varphi(T)$$

where k is the quotient of the compression ratio coefficients. $k = 2.7203\pm0.0001$) is determined based on building up equipment for laboratory-scale preparation of secondary standard gases and considering the sensitivity difference between hydrogen isotopes.

To make abundance measurements in hydrogen isotopes system more efficient, Shi Lei has modified the mass discrimination of ion optics. The following is the equation expressed by Shi Lei:[12,13,16,17]

$$\varphi(T) =$$

$$\frac{\dfrac{e^{k/6}I(T^+_2)}{\sqrt{6}F_{T_2}}+0.5\dfrac{e^{k/5}I(DT^+)}{\sqrt{5}F_{DT}}+0.5\dfrac{e^{k/4}I(HT^+)}{\sqrt{4}F_{HT}}}{\dfrac{e^{k/2}I(H^+_2)}{\sqrt{2}F_{H_2}}+\dfrac{e^{k/4}I(D^+_2)}{\sqrt{4}F_{D_2}}+\dfrac{e^{k/6}I(T^+_2)}{\sqrt{6}F_{T_2}}+\dfrac{e^{k/4}I(HD^+)}{\sqrt{4}F_{HD}}+\dfrac{e^{k/4}I(HT^+)}{\sqrt{4}F_{HT}}+\dfrac{e^{k/5}I(DT^+)}{\sqrt{5}F_{DT}}}$$

$\varphi(D) =$

$$\frac{\dfrac{e^{k/4}I(D_2^+)}{\sqrt{4}F_{T_2}}+0.5\dfrac{e^{k/4}I(HD^+)}{\sqrt{4}F_{DT}}+0.5\dfrac{e^{k/5}I(DT^+)}{\sqrt{5}F_{HT}}}{\dfrac{e^{k/2}I(H_2^+)}{\sqrt{2}F_{H_2}}+\dfrac{e^{k/4}I(D_2^+)}{\sqrt{4}F_{D_2}}+\dfrac{e^{k/6}I(T_2^+)}{\sqrt{6}F_{T_2}}+\dfrac{e^{k/4}I(HD^+)}{\sqrt{4}F_{HD}}+\dfrac{e^{k/4}I(HT^+)}{\sqrt{4}F_{HT}}+\dfrac{e^{k/5}I(DT^+)}{\sqrt{5}F_{DT}}}$$

$$\varphi(H) = 1 - \varphi(D) - \varphi(T)$$

where F is the sensitivity quotient of various species of hydrogen isotopes system, as written below:

$F(H_2) = 1$, $F_{D2} = 0.975 \pm 0.001$, $F_{T2} = 0.904 \pm 0.002$, $F_{HD} = 0.988 \pm 0.001$, $F_{HT} = 0.9395 \pm 0.002$, $F_{DT} = 0.952 \pm 0.002$.

Five different samples were designed, and four comparisons were made by four separate organizations. The analyzing results between each other are comparable within the acceptable difference. The measuring results among the labs are comparative, indicating that the analytic method is reliable.

2. Problem of computing reaction equilibrium constants in hydrogen isotope abundance measurement with low-resolution MS

Mixtures of H_2, D_2, and T_2 in the gass phase will not remain isotopically pure for a long time. The mixed molecules HT, DT, HD are rapidly formed in less than 24 h. Equilibrium is established in any concentration of all the molecular species according to the following process. The six hydrogen isotopes exchange the reactions published by Jones are shown in Table 2.[10]

Jones' calculations gave the equilibrium constants at different temperatures from 25 K to 2500 K.[10] It is important to note that all these constants are not independent, $K_1 = K_3K_4$, $K_6 = K_4K_5$, and $K_2 = K_3K_5$.

However, it is impossible to have all the equilibrium constants at different temperatures. Shi Lei have established a theory of statistical mixing. All the equilibrium constant at different temperatures can be written as follows:[12,13,16,17]

$$K_1 = 3e^{\frac{1215.38}{R}\left(\frac{1}{425.39}-\frac{1}{T}\right)} (T < 2611.81K) \qquad (14)$$

$$K_1 = 4 (T \geq 2611.81K)$$

$$K_2 = 3.84e^{\frac{158.59}{R}\left(\frac{1}{332.35}-\frac{1}{T}\right)} (T < 1151.05K) \qquad (15)$$

$$K_2 = 4 (T \geq 1151.05K)$$

$$K_3 = 1.8e^{\frac{423.67}{R}\left(\frac{1}{361.35}-\frac{1}{T}\right)} (T < 1425.25K) \qquad (16)$$

$$K_3 = 2 (T \geq 1425.25K)$$

$$K_4 = 1.6667e^{\frac{751.96}{R}\left(\frac{1}{423.66}-\frac{1}{T}\right)} (T < 2902.10K) \qquad (17)$$

$$K_4 = 2 (T \geq 2902.10K)$$

Table 2. Equilibrium constants designations for isotope exchange reactions.

$H_2 + T_2 = 2HT$	K_1
$D_2 + T_2 = 2DT$	K_2
$T_2 + HD = HT + DT$	K_3
$H_2 + DT = HD + HT$	K_4
$D_2 + HT = HD + DT$	K_5
$H_2 + D_2 = 2HD$	K_6

Table 3. Equilibrium constants for hydrogen isotopic equilibria.

T/K	K_1	K_2	K_3	K_4	K_5	K_6
2500	3.99	4.00	2.00	1.99	2.00	3.97
2000	3.98	4.00	2.00	1.99	2.00	3.97
1500	3.94	4.00	2.00	1.98	2.00	3.96
1250	3.90	4.00	1.99	1.96	2.01	3.94
1000	3.81	3.99	1.98	1.93	2.02	3.90
900	3.76	3.98	1.97	1.91	2.03	3.87
800	3.68	3.98	1.95	1.88	2.04	3.83
700	3.59	3.97	1.94	1.85	2.05	3.78
600	3.45	3.96	1.91	1.80	2.06	3.72
500	3.26	3.93	1.88	1.74	2.09	3.62
400	2.99	3.88	1.82	1.64	2.13	3.48
300	2.58	3.82	1.74	1.48	2.20	3.26
298.1	2.57	3.82	1.74	1.48	2.20	3.26
250	-	3.77	1.67	-	2.26	-
200	1.95	3.69	1.58	1.24	2.34	2.90
150	-	3.57	1.33	-	2.68	-
100	0.95	3.32	1.18	0.802	2.82	2.26
50	0.24	2.60	0.687	0.353	3.78	1.33
25	-	1.95	0.282	-	6.94	-

$$K_5 = 2.1333e^{\frac{-265.56}{R}\left(\frac{1}{413.13}-\frac{1}{T}\right)} (T < 1795.56K) \qquad (18)$$

$$K_5 = 2 (T \geq 1795.56K)$$

$$K_6 = 3.5556e^{\frac{473.99}{R}\left(\frac{1}{428.47}-\frac{1}{T}\right)} (T < 3732.02K) \qquad (19)$$

$$K_6 = 4 (T \geq 3732.02K)$$

By using equations 1-6 and considering the equation of $D_2 + T_2 = 2DT$, K_2 is expressed as follows;

$$K_2 = 3.84e^{\frac{158.59}{R}\left(\frac{1}{332.35}-\frac{1}{T}\right)} (T < 1151.05K) \qquad (15')$$

$$K_2 = 4 (T \geq 1151.05K)$$

Equations 7-10 are rewritten as follows;

$$sI(D_2^+) = \frac{(I_5)^2}{K_2 I_6} \qquad (7')$$

$$I(HT^+) = I_4 - I(D_2^+) = I_4 - \frac{I_5}{K_2} \qquad (8')$$

$$I(HD^+) = I_3 - a_{31}I(HT^+) - a_{32}I(DT^+) - a_{33}I(T_2^+) \qquad (9')$$

$$I(H_2^+) = I_2 - a_{21}I(HD^+) - a_{22}I(D_2^+) - a_{23}I(DT^+) \qquad (10')$$

Hydrogen isotopes system abundance measurements in sampling temperature is of vital importance, especially from the view point of system control in the fuel processing system of the fusion reactor. Requirements are satisfied by the new formula for computation hydrogen isotope abundances in mass spectrometry.

3. Problem of computing ratios of monatomic ions in hydrogen isotope abundance measurement with low-resolution MS

Electron bombardment of the six diatomic molecular species resulted in the formation of the three monatomic ions, on a probability basis. When pure gases were bombarded, measurements of these ions resulted in the following typical values for the particular mass spectrometer:

For H_2: $2a_{11} = I(H^+)/I(H_2^+)$

For D_2: $2a_{22} = I(D^+)/I(D_2^+)$

For T_2: $2a_{33} = I(T^+)/I(T_2^+)$

The probability of forming the monatomic ions from the heteronuclear molecular species is difficult to measure and requires further computation. Although it is generally assured for such analyses that the "cross section" for forming diatomic ions from molecules by impact of 100 ev electrons is the same for all the isotopic species, a more careful approach must be taken for monatomic ion formation.

Extending the notation used above:

$a_{12} = I(H^+)/I(HD^+)$; $a_{21} = I(D^+)/I(HD^+)$

$a_{13} = I(H^+)/I(HT^+)$; $a_{31} = I(T^+)/I(HT^+)$

$a_{23} = I(D^+)/I(DT^+)$; $a_{32} = I(T^+)/I(DT^+)$

Without analysis of the mechanics of forming these ions, there are two plausible procedures for predicting the forming of monatomic ions from the heteronuclear molecular species.[10]

a. An assumption that the difference in the ratios for the pure gases is characteristic only of the monatomic ion would indicate that $a_{ij} = a_{ii}$ for all j, $I_1 = a_{11}(2I_{11} + I_{12} + I_{13})$, etc. Such a procedure would predict for our instrument that $a_{23} = 0.0027$, which is in conflict with the value given above, but is approximately correct, and is a convenient handling of this second-order correction.

b. A more plausible assumption might be that an unsymmetrical molecule, $X_i X_j$, forms the X_i^+ and X_j^+ ions in equal amounts with $a_{ij} = a_{ji} = (a_{ij} \cdot a_{jj})^{0.5}$. It is rather tenable and probably accurate. This method was used throughout the present work.

The ratios of the following monatomic ions have been computed using the Frank-Condon principle with acceptable agreement with experimental values. In general, the absolute values of these ratios depend on the excess energy of the impact electrons above the threshold voltage for the process, and upon the physical temperature of the ion source, hence these ratios will vary between instruments. However, the ratio of the ratios can be expected to remain constant, and Schaeffer and Hastings[10] gave values that are related as follows: $a_{11} = 2.2a_{22} = 4.2a_{33}$. For simplification, R is defined as a_{22}.

$a_{11} = 2.2R$; $a_{33} = 0.53R$; $a_{12} = a_{21} = 0.74R$; $a_{13} = a_{31} = 0.50R$; $a_{23} = a_{32} = 0.38R$

From the view point of Table 4, the ratio of the ratios of experiments vary from those using the Frank-Condon principle. It is realized that these assumptions are not totally justified.

Shi Lei[12,13,16,17] revised the ratio of the ratios by volume of molecules of hydrogen isotopes using the theory of grand unification. New ratio of the ratios had been established. Following equations of the ratio of the ratios can be written as follows by Shi Lei:

$a_{11} = 1.1R$; $a_{33} = 0.795R$; $a_{13} = a_{31} = 0.935R$; $a_{23} = a_{32} = 0.892R$;

The ratio of the ratios revised by volume of molecules of hydrogen isotopes using the theory of grand unification is not in conflict with the experimental evidence.

Table 4. The ratios of the following monatomic ions measured by experimentalists home and abroad.

Experimentalist	a_{11}/%	a_{22}/%	a_{33}/%	a_{11}/a_{22}	a_{33}/a_{22}
Shi Lei,China Institute of Atomic Energy (Low-resolution MS MAT253)[16,17]	0.645	0.545	0.440	1.183	0.807
Zhang Hailu,Chinese Academy of Engineering and Physical Science (low-resolution MS MAT250)[11]	1.43	0.9	-	1.589	-
Gu Wensheng, Chinese Academy of Engineering and Physical Science (HR MS MAT271)	0.00788	0.00494	0.00496	1.595	1.004
Losalamos Sci. Lab. B.B.McInteer	0.0082	0.0055	0.0042	1.491	0.764
B.Wright and P.K.Robinson	0.503	0.382	0.100	1.317	0.262
R.Schott and G.Beau	0.5	0.4	0.4	1.250	1.000

4. Gas preparation of hydrogen isotopes standards

If suitable analyzers and accessory equipments are available, high resolution mass spectrometry should routinely analyze mixtures of the hydrogen isotopes system accurately within 0.5% under ordinary operating conditions, while low resolution MS should routinely analyze mixtures of the hydrogen isotopes accurately within 2% with accurately mixed standards.

Therfore, accurately mixed standards result in accurate MS analysis of hydrogen isotopes system. Shi Lei[12,13,16,17] reviewed various methods of hydrogen isotopes gas preparation, including gravimetry, pressure, volume, infiltration, saturation, electro analysis and didution index methods. Zhang Hailu[15] had established a gas preparation method, as illustrated by Figure 1. However, the gas preparation method worked with cryogenic active carbon flask that had the disadvantage of complex facilities, and the error of gas preparation was not been revised. Shi Lei[12,13,16,17] has established a gas preparation method of deuterium and tritium, as illustrated by Figure 2. The results showed that preparation value was valid in the relative error range of 0.02% for the gas preparation method of deuterium and tritium. $y = 1.03451x$, $r = 0.99235$, where x is abundance calculated by the manometer, and y is the demarcated abundance.
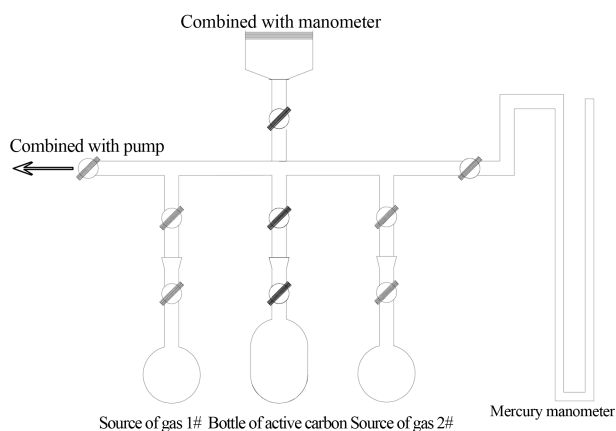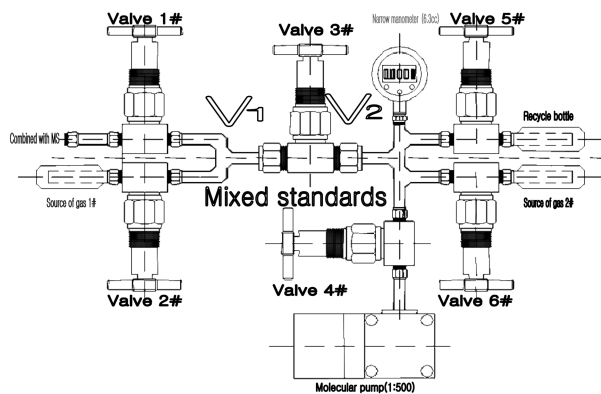

Figure 2. cheme of experimental apparatus.

Figure 2. A gas preparation method of deuterium and tritium.

5. Conclusions

MS has been employed as a rapid measurement tool for hydrogen isotope abundance. Much attention has been paid to develop fully-automated MS analysis for hydrogen isotopes system. Although both medium and high resolution MS are commercial available worldwide for hydrogen isotopic abundance measurement, a low resolution MS method for the measurement of hydrogen isotopic abundance has been investigated. In China, a series of progress were designed and made, including methodological check, computations and modifications on measurement of abundance in hydrogen isotopes system, key techniques on gas preparation of hydrogen isotopes, contrast analysis of measurement of abundance in hydrogen isotopes system, and assessment of results of measurements and applying. Some interesting results were obtained. Thanks to the improvement, the measurement precision by the low resolution mass spectrometry goes down to less than 2%.

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