Analysis of Hydrogen Isotopes in Consumer Goods Using High Precision Gas Mass Spectrometry

Jeong Eun Kim [a], Min Jun Kim [b], Bong Gi Kim [b], Jin Bok Lee [c], Jin Seog Kim [c], Kiryong Hong [c*]
[a] *Division of Nuclear Chemistry Technology, Korea Atomic Energy Research Institute (KAERI)*
[b] *Division of Radiation Regulation, Industrial Radiation Safety Department, Korea Institute of Nuclear Safety (KINS)*
[c] *Team of the Gas Isotope Analysis Standard, Gas Analysis Standard Group, Korea Research Institute of Standards and Science (KRISS)*
[*]Corresponding author: khong@kriss.re.kr

1. Introduction

Some consumer goods containing radioactive substances are in circulation and used in everyday life. Among these consumer goods, a gaseous tritium light source (GTLS) contains gaseous tritium, which uses the principle by which the beta-ray emitted by tritium stimulates a fluorescent substance to emit light [1,2]. Tritium light is similar to that of fluorescent lamps, but it has a much longer lifespan. Therefore, tritium lights are being used as a consumer product in industry and daily life because they can be operated without electricity. Due to the above-mentioned radioactive risk of tritium, consumer goods with a certain radioactivity concentration and total radioactivity are regulated in accordance with the Nuclear Safety Act. However, since most consumer goods distributed in Korea have no information that can confirm the amount of radiation, it is necessary to analyze the radiation for safety regulation.

In this study, hydrogen isotopes included in several consumer products were analyzed using a high precision gas mass spectrometer.

2. Methods

2.1 Gas Mass Spectrometer

The equipment used in this study was a precision Gas Mass Spectrometer (Gas/MS, model MAT 271, Thermo Scientific, Bremen, Germany), and its schematic diagram is shown in Figure 1. The Gas/MS can only analyze gas components, and it separates them according to the mass-to-charge ratio (m/z). A magnet designed at 90 degrees in the magnetic sector refracts ions. At this time, since the ion particles' refractive indexes differ according to their mass, they are separated according to the mass and charge ratio and reach the detector (Faraday collectors).

The detailed principle of Gas/MS is documented in several publications [3-7]. The Gas/MS measurement conditions used in this study were as listed in Table 1.

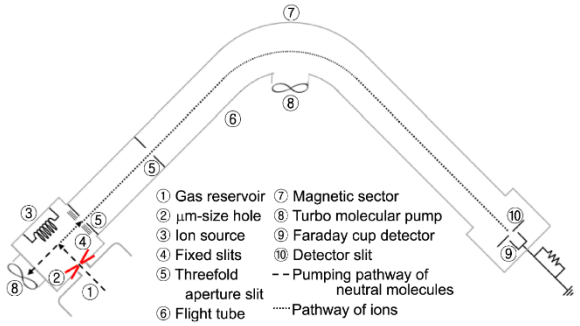

Figure 1. Internal schematic diagram showing principle of precision gas mass spectrometer model MAT271.

Table 1. Analytic condition for Gas/MS

Emission current	60 μA
Acceleration voltage	6 kV
Detector	Faraday Ⅱ
Resolution	220

2.2 Sample Injection Part

As shown in Figure 2 (b), the amount of gas injected inside was very small because of the small size of the GTLS. To analyze this, a mini chamber was manufactured by modifying the bellows valve for high vacuum (Figure 2 (a)). The mini chamber was designed to facilitate sample injection and discharge by reducing the internal volume to a minimum, and an O-ring gasket was used to block the inflow of external gas and prevent the sample from leaking. The prepared mini chamber was connected to the sample injection part of the mass spectrometer, and the GTLS sample was put into the mini chamber, as shown in Figure 2 (b). Then, close the valve of the mini chamber to break the samples.

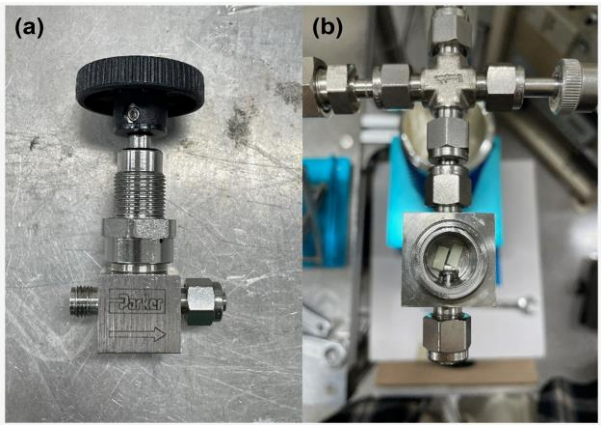

Figure 2. Mini chamber for destroying GTLS samples. (a) Photo of mini-chamber with modified high-vacuum bellows valve. (b) Inside mini chamber before sample destruction.

3. Results

3.1 Analysis Spectrum of GTLS

The spectrum analyzed for the gas component of GTLS samples is shown in Figure 3. As a result of GTLS analysis, the H_2, HD or H_3^+(T) or ^{3}He, HT or D_2 or He, DT, and T_2, which correspond to the mass-to-charge ratio (m/z) 2 to 6 and the air components were detected. Of these, the molecules containing tritium (HT, DT and T_2) were quantified in this study. The mole fraction for each component could be determined through the sensitivity of the equipment to the corresponding mass under the conditions of the above-mentioned equipment. In the case of T_2, the sensitivity of the equipment is generally obtained using a standard material, but since there is no T_2 standard gas, the sensitivity of D_2 was obtained instead. Since the measuring equipment measures the partial pressure of the component with respect to the entire sample, it is possible to determine the amount of gas for each component by applying the detected concentration ratio to the total amount of gas of the sample. The total amount of gaseous T in the sample was calculated by the ratio of the mass of tritium in the molecule to the amount of gas for each component.

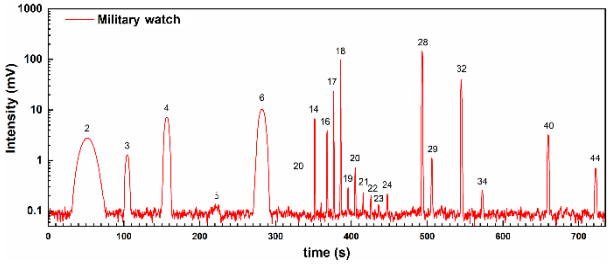

Figure 3. The spectrum of the gas component in GTLS

3.2 Quantification of gases containing tritium

Quantification of components corresponding to m/z = 3 and 4 are important to determine the total amount of tritium. However, the resolution of the equipment used in this study cannot separate HD, T, and ^{3}He at m/z = 3. Therefore, the abundances of T in m/z = 3 were determined by taking into consideration the amount of tritium in HT together with the amount of tritium in DT. Equation (1) was used to determine the amount of tritium.

$$f_T = \frac{f_{HT}}{2} + \frac{f_{DT}}{2} + \left(2 \times f_{T_2}\right) \qquad (1)$$

where f_T, f_{HT}, f_{DT}, f_{T_2} represent the mole fraction (mol mol^{-1}) of T, HT, DT and T_2 respectively. On the other hand, the amount of 3He was calculated by adding the amount calculated considering the half-life of tritium and the amount assuming a probabilistic isotope relationship between H_2, HT, and T_2. However, the amount of 3He which is calculated through these procedures is negligible as a measurement uncertainty level.

Also, at m/z = 4, ^{4}He is separated from HT and D_2, but HT and D_2 are not separated from each other. As a result of the detection, since ^{4}He was not detected, components detected at m/z = 4 correspond to HT and D_2. The amount of HT was obtained by the following formula (2).

$$f_{HT} = \sqrt{f_{H_2}} + \sqrt{f_{T_2}} \qquad (2)$$

where, f_{HT}, f_{H_2}, f_{T_2} represent the mole fraction (mol mol^{-1}) of HT, H_2 and T_2 respectively.

As a result, the total amount of gaseous tritium in GTLS determined by the above measurements and calculations is shown in Table 2.

Table 2. Gaseous tritium components in various GTLSs

Products		**Amount of gases (μg)**			**Total amount of T (μg)**	**Radiation of T (GBq)**	**Exceeding the reference value or not**
		HT	**DT**	**T_2**			
Fishig lure	A	0.619	0.00164	6.010	6.48	2.31	Excess
	B	0.214	0.00168	1.960	2.12	0.76	-
	C	0.264	0.00478	3.570	3.77	1.34	Excess

Necklace Large (Freestone)	2.54	-	32.20	34.11	12.14	Excess
Necklace Small (Freestone)	0.523	-	3.73	4.12	1.47	Excess
Tritium tube Small (Mixglo)	0.0866	-	1.06	1.12	0.40	-
Tritium tube medium (Mixglo)	0.138	-	1.37	1.47	0.52	-
Tritium tube Large (Mixglo)	0.0053	0.0053	4.92	4.93	1.75	Excess
Compass (CARMENGA)	0.99	0.00144	4.7	5.46	1.94	Excess
Watch (ADDIES)	0	0	0	0.00	0.00	Not included
Watch (Luminox)	0.125	0.00017	0.409	0.50	0.18	-
Watch (Deepblue)	0.668	0.00058	0.787	1.289	0.46	-
Watch (Marathon)	0.06485	0.00038	0.122	0.171	0.06	-
Watch (Traser)	0.0297	0.0000916	0.069	0.0912	0.03	-

4. Conclusions

A Gas/MS was used to analyze the gaseous tritium component in GTLSs. As a result, the amount of gaseous tritium in one sample ranged from 0.09×10^{-6} g to 6.48×10^{-6} g. This is a level of 0.03 GBq to 2.31 GBq when converted to the radiation unit Becquerel (Bq). Most of the product groups were found to be significantly lower than the exemption amount of tritium (1 GBq) set by the Korean Nuclear Safety Act (or the International Nuclear Safety Organization), but there were some products that exceeded this limit. Moreover, additional analysis using other equipment is required for solids and liquids with adsorbed tritium.

REFERENCES

[1] K. Kim, K. S. Kim, E.-S. Chung, S. H. Son, D.-W. Kang, K. Kim and K.-S. An, Manufacturing Process of Self-luminous Glass Tube Utilizing Tritium Gas: Optimization of Phosphor Coating Conditions, Korean Journal of Chemical Engineering, Vol.22, p. 899, 2005.
[2] M. Eisenbud, B. Bennett and R. E. Blanco, Tritium in the Environment NCRP Report No 62. IAEA: International Atomic Energy Agency (IAEA), 1979.
[3] D. Min, J. B. Lee, C. Lee, D. S. Lee and J. S. Kim, Estimation of Mass Discrimination Factor for a Wide Range of m/z by Argon Artificial Isotope Mixtures and NF_3 Gas, Bulletin of the. Korean Chemical. Society, Vol.35, p. 2403, 2014.
[4] J. Tshilongo, D. Min, J. B. Lee and J. S. Kim, Preparation of Helium Isotope-certified Reference Materials by Gravimetry, Bulletin of the Korean Chemical Society, Vol.36, p. 591, 2015.
[5] J. Y. Lee, K. Marti, J. P. Severinghaus, K. Kawamura, H. S. Yoo, J. B. Lee and J. S. Kim, A Redetermination of the Isotopic Abundances of Atmospheric Ar, Geochimica et Cosmochimica Acta, Vol.70, p. 4507, 2006.
[6] I. Yang, L. Pitre, M. R. Moldover, J. Zhang, X. Feng and J. S. Kim, Improving Acoustic Determinations of the Boltzmann Constant with Mass Spectrometer Measurements of the Molar Mass of Argon, Metrologia, Vol.52, p. S394, 2015.
[7] M. Varlam, S. Valkiers, M. Berglund, P. Taylor, R. Gonfiantini and P. De Bièvre, Absolute Isotope Amount Ratio Measurements on Gases: Part I: Measurements of Isotope Amount Ratios—Basic Theory, International Journal of Mass Spectrometry, Vol.269, p. 78, 2008.