Preparation and Validation of Gas Sealed High Isotopic Purity Heavy Water Reference Standards

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Abstract

The method for preparation of helium gas sealed high isotopic purity heavy water (D₂O) reference standards on a large scale has been amply demonstrated. The percentage purity of the reference standards has been estimated employing Fourier-Transform Infrared (FT-IR) method standardized with certified D₂O standard and confirmed by validation using the same method with supplementary certified standard having its purity value declared from a different method – Fourier-Transform Nuclear Magnetic Resonance (FT-NMR) spectroscopy, each of the certified standards having an accuracy of ± 0.01 wt.%. The work has also been extended in the preparation of high purity reference standards (99.86 wt.%, 99.90 wt.% and 99.96 wt.%) with an accuracy of ± 0.01 wt.% in stainless steel storage-containers (total 15 Nos.) in collaboration with Heavy Water Plant (HWP) laboratory, Baroda, Vadodara. The standards prepared are extremely useful for day-to-day quality control of product D₂O as well as certifying the quality of export consignments from different HWPs. This also helps all the heavy water plant laboratories in India to analyze high grade heavy water samples with same level of accuracy and reproducibility.

Keywords: D₂O; Heavy Water; H₂O; Light Water; Isotopic purity, Fourier-Transform Infrared spectroscopy; IR

Introduction

The nuclear power program in India has been conceived on optimum utilization of domestic uranium reserves for Pressurized Heavy Water Reactors (PHWRs) [1]. The inherent advantage of heavy water (D₂O) with low neutron absorption and effective moderation facilitates the use of natural uranium (0.7% ²³⁵U) as fuel in PHWRs. D₂O is basically used as a neutron moderator and coolant in PHWRs and NRU type research reactors. In the Indian context, production of heavy water and the estimation of its isotopic purity are important aspects because of its extensive use in all existing and future PHWRs. The specification for reactor grade (> 99.78 wt.%) high isotopic purity heavy water is quite rigid; a slight change in the concentration of deuterium in heavy water can alter the neutron availability in the reactor. The lowering of deuterium concentration of heavy water i.e. downgradation of D₂O in a reactor core results in loss of neutron population viz. reactivity [2, 3]. Likewise, immense care is needed while handling heavy water standards and samples because of their extreme hygroscopic nature. The storage of large quantity of heavy water standard is also equally indispensable, particularly for its high isotopic purity. Hence, stainless steel containers with helium blanket have been considered for long term storage in the process of making high purity reference standards. A series of steps have been followed here taking adequate care and protection from air ingress during the entire procedure.

Prior to the estimation of isotopic concentration of heavy water for its quality assurance, it may be remembered that D₂O is not synthesized from pure substances, rather it is prepared by separation techniques for its plant scale requirements. It is not possible to have primary D₂O standards in a strict sense. Universal standards are available only at the low (0-1 wt.%) concentration range. There are no universal standards available in the middle (1-99.5 wt.%) and high (> 99.5 wt.%) concentration ranges. Furthermore, literature suggests that the isotopic purity of heavy water can be determined with various analytical techniques [4-8], each being sensitive at different concentration ranges of D₂O. Nevertheless, most of the techniques are not absolute except some cumbersome and time-consuming methods based on density measurements. Hence, quantification and validation of reference standards is solely based on multiple measurements in a number of laboratories.
The present work reports the preparation of helium gas sealed heavy water reference standards on a large scale in the high concentration range and quantify them on application of Fourier-Transform Infrared (FT-IR) spectroscopy - one of the appropriate analytical techniques. In addition, these large-scale high purity reference standards are to be validated by the same FT-IR method (fast & precise technique) calibrated with supplementary certified D$_2$O standard having its purity value declared from a substitute method – Fourier-Transform Nuclear Magnetic Resonance (FT-NMR) spectroscopy.

**Experimental**

**Materials and method**

All the stainless steel containers were fabricated with SS-304 material for long term storage of high concentration heavy water. Each container was provided with a sample port with neoprene rubber diaphragm as shown in Fig. 1. Helium was taken as blanket gas which is to be filled through the helium inlet valve. The folded tube below the sampling port provides a long diffusion path barrier if a trace of moist air enters through the diaphragm. The high purity D$_2$O (99.97 wt.%) was supplied by heavy water production plant, DAE. Ultra pure water (>18 MΩ-cm, Milli-Q) was used as diluting agent in the preparation of reference standards at different purity levels.

**Conditioning of stainless steel containers**

Initially, Dye penetrant inspection (DPI) test was carried out to check surface-breaking defects in all the steel containers as per procedure qualified to ASME Section V [9]. All the containers were further qualified employing the hydrostatic test on application of test pressure 2.0 kg/cm$^2$ (g) for 30 minutes so as to maintain their safety standards and durability over time. Clean up of impurities inside the containers was performed by rinsing them thoroughly with de-mineralized water followed by acetone (AR Grade) to satisfactory level. Subsequently, they were taken into drying with hot air followed by dry helium gas to allow all the acetone vapors to get released. The dew point test for each of the containers has was also conducted to ensure the complete dryness. Final dew point after purging with Ultra High Purity (UHP) nitrogen was about - 40°C. Lastly leak test / pressure test has been done for each of them by introducing dry helium gas using moisture trap through the helium inlet valve and keeping them sealed to a certain pressure of 1.1 kg/cm$^2$ (g) for about 10 days. Absence of any pressure drop ensured that the containers were leak-proof. Once the containers tested leak proof, they were all set to be filled with high purity heavy water.

**Filling up of stainless steel containers**

To prepare a standard at a desired value of isotopic purity, appropriate amount of ultra-pure H$_2$O was mixed with weighed quantity of high grade D$_2$O at its known concentration in a completely desiccated plastic container separately and then purity analysis of the resultant water was carried out by FT-IR method before transferring it to a storage - steel container. A dry stainless steel tube, fitted at one end by a threaded stopper compatible to the sample port of the steel container and the other end connected to a dry rubber tube, was used in transferring the resultant heavy water from plastic container to steel container in order to minimize the aerial contact of D$_2$O. About 15 kg of the resultant heavy water was transferred into a storage container through D$_2$O rinsed rubber tube connected to the stainless steel tube-fitting with the help of nitrogen pressure. The storage steel container was closed and blanketed with helium gas to a pressure of 0.7 kg/cm$^2$(g). To fill other stainless steel containers with heavy water at different desired values of isotopic purity, the same procedure was followed. Once containers are filled with high isotopic purity heavy water, any downgrading of D$_2$O in the process of transfer and subsequent storage for long duration needs to be confirmed.

**Infra red analysis of heavy water isotopic purity**

To ensure no downgradation during the process of transfer and subsequent storage of high purity D$_2$O in stainless steel containers for long period as well, samples were collected from storage-containers with standard hypodermic dry needle and luer-lock syringe.
by puncturing the rubber diaphragm of the sample port and analyzed for isotopic purity employing FT-IR method at regular intervals. The diaphragm is self-sealing when the needle is withdrawn. Fresh calibration was made with certified D$_2$O standard. Finally the isotopic concentration of D$_2$O in the reference standards prepared was further validated by making a new calibration with the same FT-IR method using supplementary certified standard. All the FT-IR spectra were collected at room temperature (25°C) against air background on a FT-IR spectrometer equipped with high-intensity ceramic light source and DLATGS detector using a CaF$_2$-transmission cell of 0.5 mm path length by transferring each representative sample from storage container. Each FT-IR spectrum corresponds to an accumulation of 16 scans with a resolution of 4 cm$^{-1}$. For analytical purpose, all the spectra were linearly off-set at $\sim$3400 cm$^{-1}$ for IR absorption by H$_2$O + HDO as shown in Fig. 2 and the decrease in absorbance with increase in concentration of D$_2$O has been recorded. Calibration error for the response of Infrar-Red instrument with heavy water standards has also been monitored on a regular basis. The process for analysis and validation of these large-scale reference standards was continued for six months to ensure that the purity of reference standards remained unchanged at respective desired values without any downgradation. It is also to be noted here that the pressure of helium blanket gas was maintained from the commencement of the process of confirmation till their final use at 0.7 kg/cm$^2$ (g).

**Results and Discussion**

**Quantification and validation of reference standard**

The measurements of IR absorbance were repeated several times and the reproducibility of the measurements was found to be $\pm$ 0.002. Initially, the concentrations of large-scale reference standards, made at desired isotopic purity values of 99.82 wt.% & 99.86 wt.%, were estimated from a linear calibration with the correlation coefficient ($R^2$) of 0.99952 in the range of 99.82 – 99.86 wt.% as shown in Fig. 3. This calibration was generated from the certified D$_2$O standard, declared with purity value of 99.86 wt.% ($\pm$ 0.01) based on density measurement. The other large-scale D$_2$O reference standard prepared at desired purity value of 99.96 wt.% was analyzed in an alternate way by lowering the concentration of its representative sample in the above range. Subsequently, the isotopic concentrations of these three large-scale reference standards were confirmed by validation from a new calibration with the correlation coefficient ($R^2$) of 0.99946 in the range of 99.82–99.96 wt.% as shown in Fig. 4. This new calibration was produced from the supplementary certified standard, having its purity of 99.98 wt.% ($\pm$ 0.01) declared by a substitute method - FT-NMR spectroscopy. Furthermore, prior to use as working standards for quality assurance, the evaluation of uncertainty in isotopic purity estimation was made by these large-scale reference standards together with certified standards on application of linear regression model based on Gaussian distribution of variables. The resulting equation is given by

$$x(\text{wt.}\%) = -0.24955 \times y(\text{Absorbance}) + 100.06849$$

(1)
with the correlation coefficient ($R^2$) of 0.99970. Then the resulting standard uncertainty (SU) in isotopic purity estimation was calculated using the following equation:

$$SU = \frac{\sum_{i=1}^{N} (x_{ref} - x_{th})^2}{N}$$

where $x_{ref}$ is respective reference wt.% concentration of D$_2$O, $N$ denotes number of reference standards and $x_{th}$ corresponds to theoretically calculated wt.% data using Eq.(1) at each measured value of absorbance. The achieved SU viz. the reproducibility of isotopic purity estimation is found to be ± 0.002 wt.%. The prolonged analysis followed by further validation ensures the percentage purity of reference standards prepared at their respective desired values. These standards prepared on a large scale, about 15 kg each, with isotopic purity values of 99.82 wt.%, 99.86 wt.% and 99.96 wt.% are now employed as working standards in high purity range. Furthermore, these high purity working standards were employed as reference standards for quantification and validation of another set of D$_2$O standards (99.86 wt.%, 99.90 wt.% and 99.96 wt.%), about 8 kg each, jointly prepared with Heavy Water Plant (HWP) laboratory, Boroda, following the procedure described above. A separate linear calibration with the correlation coefficient ($R^2$) of 0.99941 in the range of 99.82 – 99.96 wt.% as shown in Fig. 5 has been produced employing the above working standards for the purity analysis of the new set of D$_2$O reference standards to obligate them with same degree of accuracy and reproducibility.

**Conclusion**

Helium gas sealed high isotopic purity heavy water reference standards have been prepared in stainless steel storage containers. Initially three reference standards (99.82 wt.%, 99.86 wt.% and 99.96 wt.%), 15 kg each, have been prepared and estimated their respective purity values employing FT-IR method standardized with certified D$_2$O standard, stated with purity value based on density measurement. This has been followed by validation of these reference standards using the same FT-IR method with supplementary certified D$_2$O standard, having its purity value declared from a substitute method – FT-NMR spectroscopy. Each of the certified standards considered here has an accuracy of ± 0.01 wt.%. In addition, the same procedure for preparation and validation has been well employed using these reference standards as working standards to declare the isotopic purity values of another set of reference standards (99.86 wt.%, 99.90 wt.% and 99.96 wt.%) with accuracy of ± 0.01 wt.% prepared in stainless steel storage containers (total 15 Nos.), 8 kg each, (Table 1) in collaboration with Heavy Water Plant (HWP), Baroda. The standards made here are extremely useful for day-to-day quality control of product heavy water as well as certifying the quality of export consignments from different HWPs. This also helps all the heavy water plant laboratories in India to analyze high grade heavy water samples with same level of accuracy and reproducibility.
Table 1: Purity & wt. of Reference Standards dispatched

<table>
<thead>
<tr>
<th>Heavy Water Plants (HWPs)</th>
<th>No of Standards</th>
<th>Weight of Heavy Water Reference Standards (Kg.)</th>
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<tr>
<td></td>
<td>99.86 wt.%</td>
<td>99.90 wt.%</td>
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<td>Manuguru</td>
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<tr>
<td>Thal</td>
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References