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Performance of refractometry in quantitative estimation of isotopic concentration of heavy water in nuclear reactor

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ABSTRACT

The method of refractometry has been investigated for the quantitative estimation of isotopic concentration of heavy water (D_2O) in a simulated water sample. Feasibility of refractometry as an excellent analytical technique for rapid and non-invasive determination of D_2O concentration in water samples has been amply demonstrated. Temperature of the samples has been precisely controlled to eliminate the effect of temperature fluctuation on refractive index measurement. The method is found to exhibit a reasonable analytical response to its calibration performance over the purity range of 0–100% D_2O. An accuracy of below ±1% in the measurement of isotopic purity of heavy water for the entire range could be achieved.

1. Introduction

Heavy water (D_2O) is used as a neutron moderator and coolant in presssurised heavy water reactors (PHWRs) and research reactors (Bharj et al., 2006). In its role as a moderator, heavy water does not absorb fission neutrons to any appreciable extent but significantly reduces their energy to thermal level as a result of scattering of neutrons by nuclei in D_2O. Thermal neutrons enhance the probability of fission and a controlled chain reaction can be sustained even with a very low concentration of fissile material such as natural uranium (0.7% ^{235}U). Heavy water while functioning as both moderator and coolant (Rae, 1972) is not consumed but remains in the reactor, though it can get diluted/degraded due to its hygroscopic nature. The degradation of heavy water i.e. lowering of concentration of D_2O in a reactor core results in loss of neutron population viz. reactivity (Glasstone and Sesonske, 1986). Accordingly, a very accurate and precise analysis of isotopic purity of heavy water in the core is necessary from reactivity point of view. The estimation of isotopic concentration of heavy water is also equally indispensable in D_2O production and concentration (upgradation) facilities, and in various studies involving the use of D_2O.

The literature indicates that isotopic estimation of heavy water can be performed with various analytical methods responding at different concentration ranges of D_2O. One of such methods is isotope ratio mass spectrometry that can be used as a key analytical technique particularly at low (0–1%) concentration range. This method is however generally avoided in the other concentration ranges because of memory problems. Likewise, Infrared spectroscopy appears to give considerable success to the isotopic analysis of D_2O only at low (0–1%) and high (more than 99.5%) concentrations (Kimbrough and Askins, 1969; Lappi et al., 2004; Han et al., 2005). For analysis in the broad intermediate range (1–99.5%), infrared spectroscopy deals with the use of characteristic transmission peak (Stevens et al., 1961). Nevertheless, the hurdle to be faced in this range (1–99.5%) is in separating the transmission peaks originated at a given infrared absorption region due to variation of concentration thereby making it hard to achieve higher precision and a proper calibration. Other methods like density measurement, gas chromatography employed in different ranges are also sensitive but very much cumbersome and time-consuming as well. In contrast, the method of refractometry is sufficiently simple and sensitive to be employed routinely for rapid isotopic analysis of D_2O (Baxter et al., 1911; Bertie et al., 1989; Ingelstam et al., 1954; Kalnin et al., 1990; Shukla and Udupa, 2000) over the entire range from 0% to 100%. However, there are some important factors such as control in temperature fluctuations, accuracy of measurement in refractive index etc. needed to be improved. Eventually, these factors influence in determining the percentage purity of heavy water but even then an accuracy of less than ±1% in its purity measurement is possible to be achieved in the complete range.

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The present paper aims to scrutinize the performance of method of refractometry for rapid and non-invasive determination of D_2O concentration in water samples. The method provides a measurement of refractive index of heavy water with light water as its impurity content. The refractive index of heavy water with light water as an impurity is significantly different from that of pure heavy water. The most common experimentally controllable parameters that affect a refractive index measurement of liquid are wavelength of light used and temperature of the sample. For many liquids the index of refraction decreases by approximately 0.0005 for every 1 °C increase in temperature whereas the variation for water is only about −0.0001/°C. The refractive indices of simulated heavy water samples have been measured here with the aid of a refractometer for a given wavelength of light used at a particular sample temperature. Simulated D_2O samples prepared with varying proportions of H_2O are as equivalent as real plant-samples obtained from different process systems unlike some other plant-samples containing dissolved solids, oil, organic matters etc. Temperature fluctuations have also been controlled very closely. The accuracy of measurement in refractive index of simulated D_2O samples is found to be ±0.00002. In this study, weight percentage (wt.%) as well as mole percentage (mol%) concentration of D_2O both have been used to build a calibration model over the range of 0–100%. Analytical performance by this technique is found to be reasonably useful for determining the isotopic concentration of heavy water in the entire purity range.

Fig. 1. RFM870 Refractometer (Bellingham and Stanley Ltd., Longfield Road, Tunbridge Wells, Kent TN2 3EY, UK).

2. Experimental

2.1. Sample preparation

A total of 13 samples have been prepared for the measurements over the concentration range of 0–100% D_2O. The reference standard D_2O of 99.96 wt.% (±0.01) has been obtained from Research Reactor Services Division, BARC, Trombay and appropriate amount of H_2O has been mixed with standard D_2O in the preparation of simulated heavy water samples. To minimize analytical error in sample preparation, all the samples have been prepared in significant volume using 50 ml conical flask. Ultra pure water (>18 MΩ cm, Milli-Q) has been used throughout the whole experiment.

2.2. Measurement of refractive index and data processing

Refractive index (RI) measurements have been made on a digital refractometer, RFM870 (Bellingham + Stanley Ltd., Longfield Road, Tunbridge Wells, Kent TN2 3EY, UK) equipped with artificial sapphire prism and Pt100 sensor (for monitoring sample temperature, Fig. 1). Each RI measurement has been done using the temperature control system by placing a small amount of liquid (~0.5 ml) onto the prism plate dish. All refractive index ($^{20}\eta_D$) values correspond to the D line of sodium ($\lambda = 589.3$ nm) at a particular temperature (20 °C). Prior to measurement, refractometer has been calibrated with three standard liquids supplied by B + S Ltd., UK, such as BSDC & OILDC, BSLP & OILLP and AG refractometer calibration fluids with RI values $^{20}\eta_D = 1.52256 \pm 0.000074$, $^{20}\eta_D = 1.46990 \pm 0.00074$ and $^{20}\eta_D = 1.33659 \pm 0.000026$ respectively. To build a calibration model over the range of 0–100%, D_2O concentrations both in terms of wt.% and mol% have been considered. RI ($^{20}\eta_D$) data measured for simulated samples on variation of concentration of D_2O have been analyzed using ORIGIN (Origin Lab Corporation, One Roundhouse Plaza, USA) software. Data from RI ($^{20}\eta_D$) measurements on 13 samples have been divided into two complementary sets. 7 RI data have been used for calibration and 6 RI data for the prediction set (validation set), together validating the measurement-analysis protocol.

3. Results and discussion

3.1. Features for refractive index measurement

The refractive index of liquids changes significantly with temperature. It is important that the temperature of a sample is to be constant throughout its mass before an accurate reading can be taken. The sapphire prism together with the sample dish and lid over it can help in achieving optimal thermal conductivity and low-volume containment of the sample. This enables rapid thermal equilibration with the prism surface and subsequent temperature stability of the sample for the entire duration of the reading. A highly stable optical system coupled with a thermally self-regulating detection system with enhanced resolution provides accurate reading in the shortest possible time. An intelligent electronic control system coupled with a twin-probe sensor, which accurately pinpoints the prism surface temperature, enables the system to achieve and maintain the sample at the prescribed temperature. A powerful system of Peltier devices and thermal insulation ensures rapid attainment of sample target temperature. A separate multiple probe system continuously monitors the internal environment of the instrument and actively compensates any thermal fluctuation to optical and detector components. Performance of the instrument is described in Table 1.

3.2. Quantitative calibration

The measurements of refractive index have been repeated several times and the reproducibility of the results is found to be ±0.00002. The measured refractive index of pure water (H_2O) is 1.33299 ± 0.00002 at 20 °C for $\lambda = 589.3$ nm. To test the performance of method of interest, RI ($^{20}\eta_D$) data with same degree of accuracy measured for simulated samples on variation of