1. INTRODUCTION

The accuracy in internal dose assessment for occupational workers who get exposed to various radio-nuclides depends primarily upon the bio-kinetic models for these radionuclides. The earlier biokinetic models of various radionuclides have been described in ICRP Publication 30 (ICRP, 79) and were recently updated and revised in ICRP Publication 69 (ICRP, 94). These models predict the systemic uptake of various radio-nuclides that enter human body through different routes and also their subsequent removal in urine, through blood serum which serves as the fluid medium for such biokinetic processes. It was therefore considered pertinent to estimate the excretion ratio (the fraction that is excreted daily through urine to that present in serum pool of an individual) for both thorium and uranium in workers getting exposed to these two radionuclides and compare the observed and expected excretion ratio calculated on the basis of New Biokinetic Models of Th & U (ICRP, 94).

In view of the extremely low concentrations of Th & U in blood serum (<1.0 ppb), highly sensitive analytical methods using radiochemical neutron activation analysis (RNAA) technique, were developed for measuring their concentrations in urine and blood serum samples. These methods have the additional advantage of negligible reagent blank.

The daily urinary excretion of Th & U and their concentrations in blood serum of occupational workers who were continuously exposed to their Y class compounds were determined simultaneously. These data were utilised to obtain the excretion ratios for the two radionuclides, which were then compared with those expected on the basis of New Biokinetic Models.

2. MATERIALS AND METHODS

2.1 Sample Collection

The occupational subjects of this study, worked in thorium & uranium plants, and were continuously exposed to Y class Th and U compounds (exposure period 15-30 Y). Thorium plant processes Th hydroxide to manufacture Th nitrate & Th oxide. Some of the intermediate compounds of Th are thorium sulfate and thorium hydrocarbonate. Uranium plant carries out chemical separation to process uranium hexafluoride to manufacture uranium oxide fuel. These subjects work in three shifts, round the clock, and are rotated in various departments. They are regularly screened for their thorium & uranium burdens respectively using in-vivo counting and bioassay monitoring. Usually, they are kept away from the plant work two days prior to monitoring, to allow for the transient activity to clear out.

About 25 ml blood samples were collected on the first day and 16 hours (overnight) urine samples were subsequently collected on two consecutive days. Five ml of electronic grade concentrated HNO₃ was added to each of the urine samples to ensure that there was no adsorption of Th & U present in the urine samples on to the walls of the collection bottles.

When collecting biological samples for analysis of elements present in concentration levels of parts per billion (ppb), a high degree of caution needs to be exercised during collection, preservation and preparation of the samples to avoid errors due to extraneous contamination. These problems and the precautions required to avoid contamination have been discussed in detail by Sansoni and Iyenger (1979). Thorium & uranium concentration in serum is more than one million times lower as compared to its level in dust. Therefore, special precautions were taken to collect the blood serum samples in extra clean glass wares which were previously cleaned by soaking in Electronic Grade nitric acid (HNO₃) and then rinsed with triple distilled water and finally dried in dust free chambers.

2.2 Processing of the samples

The blood samples were allowed to coagulate and 10 ml of serum was separated after centrifugation, which was then dried in low heat (50-60°C) under infrared lamp on Clean Filter Bench. The residue was powdered with a perspex rod and sealed in pre-cleaned polyethylene.
To the urine samples (which measured 300 to 1000 ml), 50 ml concentrated electronic grade HNO₃ was added and allowed to digest on low heat (<100⁰C) for 2-3 hours. From the urine sample, Th & U were co-precipitated first with Ca phosphate. Whereas Th present in calcium phosphate precipitate was re-precipitated with Ca oxalate, U is kept along with Ca phosphate precipitate. Both Ca oxalate and Ca phosphate precipitates which carry Th and U quantitatively, were dried under infrared lamp and then sealed in clean polyethylene for irradiation.

2.3 Irradiation

These samples were irradiated along with their respective standards of Th or U, in swimming pool type APSARA reactor, for 14 hours in thermal neutron flux of 10¹³ n cm⁻² s⁻¹. On irradiation, thorium (²³³Th) present in the sample is converted into ²³³Pa and uranium (²³⁸U) into ²³⁹Np by (n,γ) reaction.

2.4a Estimation of Thorium-Chemical Separation of ²³³Pa and Gamma Counting

After one week of cooling (decay), the irradiated serum samples and Ca oxalate ppt. containing ²³³Pa was digested in concentrated nitric acid. Then the ²³³Pa was co-precipitated first with MnO₂ and then with BaSO₄. The BaSO₄ precipitate was subsequently filtered, dried and counted for 16h for the characteristic gamma lines of ²³³Pa (311.8 keV) using 54 cc hyper pure Ge detector. The details of the analytical procedure are discussed elsewhere (Dang et al. 1989). The irradiated Th standard was also processed in a similar manner and counted in the same geometry. Th concentration was obtained by comparing the sample and standard counts after application of due correction for chemical yield. The minimum detection limit (MDL) of 0.05 ng Th (0.2 μBq of ²³²Th) could be obtained using this method.

2.4b Estimation of Uranium - Chemical Separation of ²³⁹Np and Gamma Counting

After 2 days cooling, the irradiated serum samples and Ca phosphate ppt. containing ²³⁹Np were digested in concentrated nitric acid along with known amount of ²³⁹Np tracer. Np was then separated chemically, first using anion exchange column and then co-precipitated with BaSO₄. The BaSO₄ precipitate was filtered, dried and counted for 16h for the gamma lines of ²³⁹Np (227.5 keV and 278 keV) and ²³⁸Np (984 keV) using 54 cc HPGe detector. The details of the analytical procedure are given elsewhere (Pullat, 1994). The irradiated U standard was also processed in a similar way and was counted in the same geometry. U concentration was obtained by comparing the sample and standard counts after application of due correction for chemical yield. The minimum detection limit (MDL) of 0.2 ng U (1 μBq of ²³⁸U) could be achieved using this method.

2.5 Quality Control Analysis

The urine samples were spiked with known amount of Th and U, and then analysed by following the complete procedure of pre-concentration of Th & U from urine till the final quantification. The Standard Reference Materials (NIST, USA) such as Orchard leaves, Citrus leaves, Oyster tissues and Pine needles were also analysed for Th & U using the analytical method employed for this study.

3. RESULTS AND DISCUSSION

Average recovery obtained for the urine samples spiked with known amount of Th & U was about 90% with standard deviation of less than 5% for both of them, which indicated good reproducibility of the determinations. The results of the analysis of Standard Reference Materials (NIST, USA) are shown in Table 1. It may be noted that the values obtained using the present methods, agreed well with the certified/reported values available in the literature.

A study of correlation for both Th & U concentration in blood serum of occupational workers and their corresponding daily urinary excretion was carried out. A statistically significant linear correlation (p<0.01) between the concentration in blood serum and the corresponding daily urinary excretion was obtained.

The median concentration of thorium in blood serum and its daily urinary excretion for a group of Th plant workers was estimated as 0.80 mBq L⁻¹ and 0.36 mBq d⁻¹ respectively. Similarly, the median concentration of uranium in blood serum and its daily urinary excretion for a group of U plant workers was estimated to be 6.72 mBq L⁻¹ and 15.75 mBq d⁻¹ respectively. The total volume of serum in the body of an average Indian adult is reported to be 2.5 L (Banergee and Sen, 1958). Using this value of
blood serum volume, the total burden of thorium & uranium in serum of Th & U plant workers was estimated to be 2.01 and 16.75 mBq respectively.

3.1 Excretion Ratio of Thorium and Uranium

The ratio of daily urinary excretion of an element to that present in serum pool is termed as excretion ratio for the element. From the daily urinary excretion and serum burden values, excretion ratios of Th and U were estimated to be 18 & 92 % respectively. The mean and median values of serum burden along with the daily urinary excretion and excretion ratio for thorium and uranium for plant workers are shown table 2.

The metabolic models of Th & U predict the systemic uptake of the radionuclides entering the human body through different routes and their subsequent removal in urine through blood serum, the fluid medium for such biokinetic processes.

According to new metabolic model, thorium activity leaves the transfer compartment with a half life of 0.25d. Of the activity leaving this compartment, 8% is removed directly or through urinary path to urine; 20% is assigned to cortical bone surface, from which half goes to cortical volume & half to cortical marrow and removed with a half life of 23Y in circulating system; 30% to trabecular bone surface from which half of it goes to trabecular volume & other half to trabecular marrow and removed with half life of 4Y; 5% to the liver from which 50% is removed with half life of 9Y, 25% with a half life of 1Y into the circulating system and remaining 25% removed into faeces via GI Tract; remaining goes to other soft tissue, from which most of the activity returns back to transfer compartment (except 2% which permanently remains there). The activity going to transfer compartment is redistributed as earlier. In ICRP publication 69 (ICRP, 94), the new metabolic model of Th predicts that the daily urinary excretion of thorium is about 17% of the blood content.

Similarly, uranium activity entering the blood (transfer compartment) is rapidly excreted in urine or taken up by tissues. Of the activity leaving this compartment, 75% is removed directly or through urinary path to urine; 6.7% is assigned to cortical bone surface, from which half of it goes to cortical volume & other half return back to circulation with half life of 5 d; 8.3% to trabecular bone surface from which half of it goes to trabecular volume & other half return back to circulation with a half life of 5 d; remaining goes to other soft tissue, from which most of the activity returns back to transfer compartment (except 0.3% which clears with a half life of 100Y). The activity going to transfer compartment is redistributed as earlier. Although, the percentage of U in blood serum pool which is excreted daily, is not given in ICRP, it is clear from the new metabolic models.

Table 1: Analysis of Thorium & Uranium in Standard Reference Materials

<table>
<thead>
<tr>
<th>Reference Material</th>
<th>Concentration (ng g⁻¹) of Thorium</th>
<th>Certified value/Literature value</th>
<th>Concentration (ng g⁻¹) of Uranium</th>
<th>Certified value/Literature value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present work</td>
<td></td>
<td>Present work</td>
<td></td>
</tr>
<tr>
<td>Bovine Liver (SRM 1577)</td>
<td>60.0±5.0</td>
<td>64.0±7.0</td>
<td>0.9±0.2</td>
<td>0.8±0.3</td>
</tr>
<tr>
<td>Citrus Leaves (SRM 1572)</td>
<td>13.4±1.1</td>
<td>15.0±4.0</td>
<td>32.0±3.0</td>
<td>31.0±2.0</td>
</tr>
<tr>
<td>Pine Needles (SRM 1575)</td>
<td>35.1±4.3</td>
<td>37.0±3.0</td>
<td>17.5±2.0</td>
<td>20.0±4.0</td>
</tr>
<tr>
<td>Oyster Tissue (SRM 1566a)</td>
<td>38.0±2.0</td>
<td>40.0</td>
<td>119±15</td>
<td>132±12</td>
</tr>
</tbody>
</table>
Table 2: Thorium and Uranium Burden in Blood Serum and their Daily Urinary Excretion Ratio for a Group of Th & U Plant Workers

<table>
<thead>
<tr>
<th></th>
<th>Serum Burden (mBq)</th>
<th>Urinary Excretion (mBq)</th>
<th>Excretion Ratio (%)</th>
<th>Measured</th>
<th>Expected (Based on NewICRP Model)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thorium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>0.30 - 10.10</td>
<td>0.10 - 1.60</td>
<td>5.0 - 39.9</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Mean ±SD</td>
<td>2.63 ± 2.20</td>
<td>0.36 ± 0.29</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Median (SGD)</td>
<td>2.01 (2.14)</td>
<td>0.36 (1.74)</td>
<td>17.9 (1.6)</td>
<td>17.0</td>
<td></td>
</tr>
<tr>
<td><strong>Uranium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>1.28 - 135.9</td>
<td>1.24 - 128.4</td>
<td>43 - 307</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Mean ±SD</td>
<td>28.8 ± 32.7</td>
<td>24.1 ± 23.0</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Median (SGD)</td>
<td>17.3 (3.0)</td>
<td>15.9 (2.6)</td>
<td>92 (1.8)</td>
<td>98</td>
<td></td>
</tr>
</tbody>
</table>

No. of Thorium Plant Subjects: 24
No. of Uranium Plant Subjects: 39

model of U, that out of the total U entering the transfer compartment and subsequently the systemic compartment, about 2% is cleared with a half life of 5 years or more, and rest of about 98% is expected excreted to be either directly or indirectly through urine.

A comparison of the estimated median excretion ratios of Th & U in occupational workers with those expected on the basis of their new metabolic models is also shown in Table 2. The estimated median excretion ratios of 18% & 92% for Th & U in occupational workers are quite comparable with those of 17% and 98% expected on the basis of new metabolic model.

4. CONCLUSIONS

The excretion ratios for occupational subjects working in Th & U plants were estimated to be 18% and 92% which are comparable with the expected values of 17% and 98% based on their new metabolic model. The study showed that the new models are quite realistic and could be effectively applied for the accurate assessment of internal radiation dose to the radiation workers exposed to Th & U & their compounds.

REFERENCES

