ASSESSMENT OF THORIUM EXCRETION IN URINE BY MEANS OF ICP-MS

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INTRODUCTION

Thorium is a primordial element with only radioactive isotopes. It is quite ubiquitous in the earth's crust and small amounts are present in foodstuffs and also in the human body. Whereas ingestion is the main pathway of uptake in non-exposed subjects, incorporation due to occupational exposure occurs most probably by inhalation. A number of industrial applications of thorium are known e.g. in heat resistant materials, welding rods, gas mantles, Mg/Th alloys, thermistors, catalysts etc. Therefore, adequate monitoring of exposed workers is required. Due to its physical characteristics as alpha-emitter and its biokinetic behaviour following incorporation, ^{232}Th is considered as one of the radionuclides with the highest radiotoxicity. Among the methods available for monitoring of the internal thorium content, whole body counting or urine analysis by alpha spectrometry proved to be inadequate to comply with the required detection limits. Interpretation of results of faecal analysis is aggravated by the variation of thorium excretion from natural intake. Up to now, basic data on dietary thorium content and in particular its biokinetics in humans is rather limited. E.g. for the intestinal uptake, the ICRP has adopted an f_1-value of $2 \cdot 10^{-4}$ in its publications N°30 (1) and N°54 (2) and of $5 \cdot 10^{-4}$ in its publications N°56 (3) and N°69 (4). But combining data of Beyer (5) and Riedel (6), for Germany an f_1-value of at least $4 \cdot 10^{-3}$ has to be assumed even under neglect of any endogenous faecal excretion or body accumulation of thorium in adults.

ICP-MS provides a tool for rapid measurement of very low concentrations of thorium in biological fluids. Therefore, in this study the feasibility and sensitivity of ICP-MS for the assessment of renal thorium excretion was investigated. Variation of urinary thorium content was studied in a group of non-exposed persons as well as its day to day variation in a particular subject.

SUBJECTS

A total of 18 healthy volunteers (7 males: mean age 46 ± 11 years (MV ± SD), range 30 to 57 years; 11 females: mean age 42 ± 23 years, range 17 to 84 years) were included in the study. None of them had a history of previous occupational exposure to thorium. The subjects were asked to collect urine for 24 hours under normal habits in polyethylene bottles. After addition of 50 ml/l conc. HNO_3 the urine was stored at 4°C until measurement. Additionally, in one of the subjects complete urine was collected for 6 consecutive days.

PROCEDURE

For the measurements an ICP mass spectrometer ELAN 5000 (Perkin Elmer Sciex) coupled to an AS90 sample changer (Perkin Elmer) was employed. Unprocessed urine was

pumped at a rate of about 0.9 ml/min to a Ryton Chamber. In all measurements a conventional GemTip cross flow nebulizer was used. The plasma flow was set to 15 l/min, the nebulizer flow to 0.95 l/min and the auxiliary flow to 0.8 l/min. Rhenium (^{103}Rh) was taken as internal standard. Standard solutions for thorium and rhenium were obtained from SPEX Ind./USA. Only ultrapure water (Milli-Q, Millipore) and nitric acid distilled by subboiling were required for the analysis. For the determination of thorium concentrations in the urine samples the method of standard additions was employed. Under these conditions a detection limit (3 SD of background signal) of 4 μBq/l urine was achieved for ^{232}Th.

RESULTS

The mean urine volumes obtained for males and females of 1.6 ± 0.5 l and 1.3 ± 0.7 l respectively were in the expected range. For all subjects investigated the mean daily ^{232}Th excretion is 25 ± 14 μBq/day, for males it is 33 ± 14 μBq/day (range 17 to 54 μBq/day) and for females it is 21 ± 9 μBq/day (range 9 to 42 μBq/day). The difference between males and females is statistically not significant. Moreover, the results obtained so far show no clear dependence of ^{232}Th excretion on age (Fig.1). The day to day variation of renal thorium excretion in one subject during 6 consecutive days is shown in Fig.2. The values obtained range from 21 to 52 μBq/day with a mean of 35 μB/day.

DISCUSSION

The interpretation of data obtained for excretion analysis of workers occupationally exposed to primordial radionuclides requires basic knowledge on the natural content and its variation of these radionuclides in faeces and urine. Due to the low f_1-value almost all thorium ingested with food is excreted in faeces i.e. faecal monitoring of occupational thorium exposure is limited by the fluctuations of Th intake from natural sources. Because of the biokinetic behaviour of Th the urinary excretion seems to be more closely related to the Th body content and may therefore be a better measure of occupational Th incorporation. But up to now, only few data are available on urinary Th content of non-exposed persons. Applying 48 h urine collections and alpha spectrometry with 10,000 minutes measuring time, Riedel (6) could obtain a mean excretion of 30 μBq Th per day in normal urine which is in good agreement with the data found in this study. Concentration of ^{232}Th was measured by Dang (7) in the urine of 11 non-exposed subjects by means of neutron activation analysis. From his data a mean daily excretion of 16 ± 6 μBq Th can be derived if a mean volume of 1.4 l urine per day is assumed. The same technique was applied by Hewson (8) on five subjects without history of occupational thorium exposure. While for two of the subjects the urinary thorium concentration was below the detection limit of 4 μBq/l, the mean daily urinary ^{232}Th content of the other three subjects can be estimated at 29 μBq.

Both methods i.e. alpha spectrometry and neutron activation analysis require careful sample processing. They are time-consuming techniques. In contrast, measurements by means of ICP-MS are carried out within few minutes without sample work-up. Moreover, the method shows a good sensitivity and reproducibility for the assessment of thorium concentration in urine. Therefore, the application of ICP-MS offers an attractive alternative for monitoring of thorium body burdens in occupationally exposed subjects and also in larger groups of the general population.

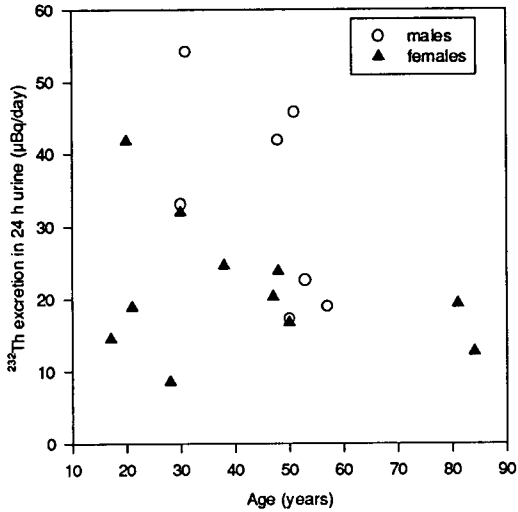

Figure 1. ^{232}Th excretion in 24 h urine in unexposed subjects.

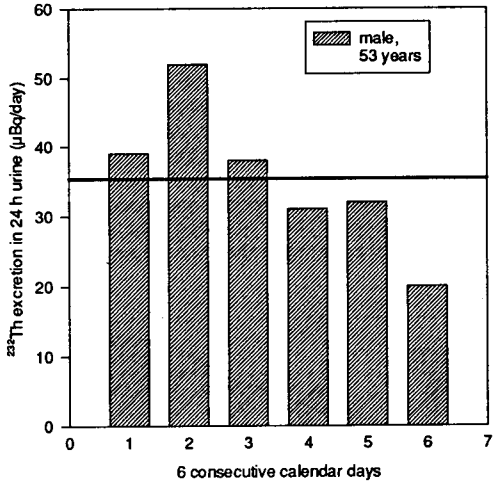

Figure 2. Intra-individual variation of urinary ^{232}Th excretion in a healthy male subject

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