Simultaneous determination of Ni, Nb, U and Th in urine and fecal samples using ICP-MS

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Abstract
Simultaneous determinations of nickel, niobium, uranium and thorium have been performed in biological material as urine and feces utilising the Inductively Coupled Mass Spectrometry (ICP-MS) technique of analysis. Among the spectroscopic methods for multielementar analysis the mass spectrometry is the only technique that can offer easily interpretable spectra, suitable resolution and low detection limits, which allows the determination trace elements in a complex matrix. In this work the chemical procedures used were the direct dilution of urine samples and the dry ashing before wet mineralisation of fecal samples. The principal requests for the analysis performance are the maximum sample dissociation and the production of monovalent ions. The urine samples were diluted 1:20 with HNO₃ 1N prepared from hyperpure HNO₃ and H₂O mili Q. The feces were dry ashed at 600°C, wet ashed with 10 mL of hyperpure HNO₃ and diluted with HNO₃ 1N. Standard solutions of talium and indium were added in each sample as internal tracers. The interference of calcium in the nickel analysis was determined and subtracted. The detection limits for Ni, Nb, U and Th were respectively 5.44x10⁻⁴ mg/L, 4.86x10⁻⁵ mg/L, 1.95x10⁻⁵ mg/L and 7.41x10⁻⁵ mg/L. The urine samples used for the determination of Ni, Nb, U and Th concentrations were collected from 68 non-occupationally exposed inhabitants from Rio de Janeiro City, Brazil, of both sexes and age range 7-51 years. Background feces samples were from people in the age range of 22-58 years. The results obtained for excretion of Ni are in agreement with the ICRP published values. The values determined for U and Th excretion in urine and feces are in concordance with other obtained values in Brazil using other analytical techniques. The values for Nb excretion in urine and feces are 2 orders of magnitude below those published for the ICRP reference man.

Introduction
The simultaneous determination of large number of elements in biological samples using a unique analytical technique is a challenge for routine bioassay monitoring programs. Among the suitable spectroscopic methods for multielementar analysis, mass spectrometry is the only one that can offer easy spectra, suitable resolution and low detection limits to determine trace elements in a complex matrix. In the ICP-MS system, the results are obtained by the combination of an inductively induced plasma coupled with a mass spectrometer. The principal request for the analysis performance is that the sample be dissociated as much as possible and the production of monovalent ions (1). The urine samples for determination of Ni, Nb, U and Th concentration were collected from 68 non-occupationally exposed inhabitants from Rio de Janeiro City, Brazil, of both sexes and ages in the range 7-51 years. The feces samples used for Ni, Nb, U and Th analysis were collected from a group of workers, of both sexes, with ages varying between 22 and 58 years, involved in mining activities in the centre of Brazil. These workers were divided in two groups: (a) the workers from Ni mining and (b) the workers from Nb mining. These results were obtained as part of a larger study of Ni, Nb, U and Th in occupationally exposed workers. Only the background
data of this study are presented in this paper, with the aim of showing the utility of the ICP-MS technique. The group (a) was considered a good background for fecal excretion of Nb, U and Th due the absence of these elements in the Ni mine. In the same way the group (b) was considered a suitable background for Ni fecal excretion

Materials and methods

Instrumentation
This study was carried out using an ICP-MS Perkin-Elmer/Sciex ELAN 5000. The equipment was projected for multielementar quantitative determinations of trace elements and isotopic composition (2). This equipment gives analysis results with detection limit between 0.1 and 0.01 ppb (µg/L) for the majority of elements in solution. The instrument was equipped with a plasma torch and a mist generator to introduce the samples. The ICP-MS is controlled by a computer through a software package, which also serves to process the data and calculate the results.

Sample Collection
To determine the nickel, niobium, uranium and thorium concentrations, biological samples (urine and feces) were collected. The urine samples were collected in plastic bottles previously washed and rinsed with miliQ water. We asked to collect the first morning excretion. The feces were collected in plastic containers previously washed and rinsed and the people were instructed to collect a complete excretion.

Sample Preparation
In this work, all the urine and feces analyses were done using an ICP-MS, using direct dilution (urine) and dry ashing and dissolution (feces), without chemical separation. The urine samples were diluted 1:20 with HNO₃ 1N, prepared from hyperpure HNO₃ and H₂O miliQ. The fecal samples were dry ashed initially at 400°C, homogenised and then dry ashed again at 600°C. From the residue 0.01g were taken, wet mineralised with 10 mL of concentrated HNO₃ and dissolved in 20 mL of 1N HNO₃ prepared from concentrated HNO₃ hyperpure and H₂O miliQ. In all the solutions which were analysed by ICP-MS, internal standards of In and Tl were added.

Results and Discussion

Urine samples
The nickel concentration results in urine were in the interval of 2-16 µg/L. To evaluate the possibility of correlation between the nickel concentrations in urine and the independent parameters sex and age, a statistical multiple regression test was applied. The test result showed no correlation between the variables (p>0.05). The results obtained in this study were compared to the ICRP standard man reference value of 7.9 µg/L (3). The t-Student test was applied and no difference between the urine concentration in Rio de Janeiro and the international reference was found (p>0.05) (4, 5). Figure 1 represents the concentrations of nickel in urine obtained in the group of Rio de Janeiro.

The niobium concentrations in urine were around 1 µg/L. The possibility of correlation between the niobium concentration in urine with the parameters sex and age was investigated through a statistical multiple regression test application. The test result showed no correlation between the urine concentration and sex or age (p>0.05). The concentration in the Rio de Janeiro group was checked against the international reference value of 257 µg/L (3). The t-Student test was not
applied because the difference between the urine concentration in Rio de Janeiro and the international reference was around two orders of magnitude. In Figure 2 the niobium concentrations in urine from the Rio de Janeiro group are shown.

**Figura 1.** Nickel excretion in urine for the Rio de Janeiro inhabitants

**Figura 2.** Niobium excretion in urine for the Rio de Janeiro inhabitants
The uranium concentration results in urine were in the interval of 0.01 and 0.12 µg/L. To evaluate the possibility of correlation between the uranium concentrations in urine with the independent parameters of sex and age, a statistical multiple regression test was applied. The test result showed no correlation between the variables (p>0.05). The concentrations in the control group were compared to the values of uranium excretion in urine found in another study conducted in Brazil (6). The Student t-test was applied and no difference between the uranium in urine concentration in the two works with inhabitants of Rio de Janeiro was found (p>0.05) (4, 5). Figure 3 shows the concentrations of uranium in urine obtained in the group of Rio de Janeiro.

![Figura 3. Uranium excretion in urine for the Rio de Janeiro inhabitants](image)

The thorium concentration results in urine were in the interval of 0.08 and 0.28 µg/L (0.33 and 1.17 mBq/L). Using the same methodology, the first step was to determine the possibility of correlation between the thorium concentrations in urine with the independent parameters sex and age, a statistical multiple regression test was applied. The test result showed no correlation between the observed parameters (p>0.05). There are few references of thorium excretion in populations. The results obtained in this work are higher than the others published for non exposed populations (7), although another study conducted in Brazil (8) presented results of same magnitude. In Figure 4 the concentrations of thorium in urine obtained in the group of Rio de Janeiro are presented.

**Feces samples**

The nickel concentration results obtained in fecal samples from a group of workers not occupationally exposed to nickel and nickel compounds were in the interval of 50-140 µg/g ash.
To evaluate the possibility of correlation between the nickel concentration in feces with the independent parameters sex and age, a statistical multiple regression test was applied. The test result showed no correlation between the variables tested (p>0.05). The concentrations in the study group were compared to the international ICRP reference value of 370 µg Ni/day [4]. The t-Student test was applied and no difference between the feces concentration from the group studied and the international reference was found (p>0.05) (4, 5). Figure 5 represents the

Figura 4. Thorium excretion in urine for the Rio de Janeiro inhabitants

Figura 5. Nickel excretion in feces for background group (Nb mine workers).
concentrations of nickel in feces obtained in the group of workers not occupationally exposed to nickel and nickel compounds.

The niobium concentration results in feces from a group of Ni mine workers, that were not occupationally exposed to Nb were around 0.8 µg/g ash (3.2 µg/day). The possibility of correlation between the niobium concentration in feces with the independent parameters sex and age was investigated through a statistical multiple regression test application. The test result showed no correlation between the niobium feces concentration and sex or age (p>0.05). The concentration in the feces of non exposed workers was discrepant with the international value of 354 µg/day (3). The t-Student test was not applied because the difference between the Nb feces concentrations in the studied group and the international reference was around two orders of magnitude. Figure 6 represents the niobium concentrations in feces obtained in this work.

![Figure 6. Nb excretion in feces for background group (Ni mine workers).](image)

The uranium concentrations in feces samples from Ni mine workers that were not occupationally exposed to uranium were around 0.5 µg/g ash (2 µg/day). To evaluate the possibility of correlation between the uranium concentrations in feces with the independent parameters sex and age, a statistical multiple regression test was applied. The test result showed no correlation between these variables (p>0.05). Figure 7 shows the concentrations of uranium in feces obtained in the group of Ni mine workers.

The thorium concentration results in feces samples from Ni mine workers that were not occupationally exposed to thorium were around 0.4 µg/g ash (1.6 µg/day). Using the same methodology, the first step was to determine the possibility of correlation between the thorium concentrations in feces with the independent parameters sex and age, applying a statistical multiple regression test. The test result showed no correlation between the parameters (p>0.05). There are few references of thorium excretion in a population, but these results are in good agreement.
with the results of other studies conducted in Brazil (8). Figure 8 shows the average concentration of thorium obtained in feces.
**Discussion and conclusions**

The ICP-MS technique is a rapid, sensitive and accurate analytical technique for the measurement of nickel, niobium, uranium and thorium in excretion samples. It can be used with the purpose of toxicological analysis in samples from individuals of the public or from occupationally exposed workers. The practical aspect of the work with ICP-MS is shown in the urine sample preparation, which only requires direct dilution. This is important when relevant information is required rapidly.

The obtained values of Ni found in urine of Rio de Janeiro inhabitants and in feces of Brazilian Nb mine workers group are in good agreement with those published internationally. The determined values of U and Th excretion in urine and feces are in concordance with values obtained values in Brazil using other analytical techniques. The values determined for Nb excretion in urine and feces are 2 orders of magnitude below those published for the reference man (3).

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**References**


