

EVALUATION OF HAND-HELD GAMMA SPECTROMETRY INSTRUMENT AS CONFIRM TECHNIQUE FOR ENVIRONMENTAL ANALYSIS OF THORIUM IN SOIL

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ABSTRACT

Gamma spectrometry hand-held instrument may show considerable analytical performances and even if they are not specifically taught for quantitative environmental analysis, in this work we evaluate the performance of one of them in this field comparing the results with ICP-MS, the reference technique in this field. In our work we want to evaluate the possibility to use the analytical performances offered by a portable gamma spectrometer as confirmatory technique.

We used for this test soils contaminated with thorium, an increasing interest pollutant, widely present in natural sediments and also emitted in environment by several anthropogenic processes such modern agricultural practices, industrial and military application. Thorium is expected also to increase in interest, for its possible exploitation as nuclear fuel instead of uranium by some countries.

KEYWORDS:

Thorium, ICP-MS, hand-held gamma spectrometry, radionuclide pollution.

INTRODUCTION

Contamination by radioisotopes can represent a problem for human and environmental safety [1, 2, 3, 4].

Thorium is a naturally-occurring, radioactive metal of the actinide series that occurs mainly in

mineral thorium phosphate monazite composed of thorium phosphate and 12% thorium oxide [5]. It is surprisingly abundant in the earth's crust, being three times more common than uranium and about as lead [6].

Thorium is ubiquitous, its release in environment occurs both from natural and anthropogenic sources that elevate its level over the background. Windblown dust [7] and volcanic eruptions are two important natural sources of thorium in the air, while mining, milling, tin processing, phosphate rock processing, phosphate fertilizer production, coal fired utilities are main human source, minor amount can become from agricultural activity [8] from military activity where was used for its low toxicity till nineties as simulant of plutonium in training activities [9], and as tracker for missiles. In future, a steeply rise of mining and industrial activities related to thorium is expected, owing to the interest in its exploitation as nuclear fuel instead of uranium by some important countries [10, 11].

More than 99% of thorium exists as ²³²Th, its most stable isotope, which undergoes α decays. This radioisotope has a half-life of around \approx 14 billion years (Table 1), thus the radioactivity of thorium is limited. Most of the other thorium isotopes are part of the decay chain of thorium and uranium (Figure 1); they are much more radioactive, but their fraction is negligible if compared to the ²³²Th. Even if thorium shows a negligible

TABLE 1
Thorium isotopes.

| Isotope | Half-life period | Emitted radiation | Energy (MeV) | Decay product |
|-------------------|----------------------------|-------------------|--------------|-------------------|
| ²²⁶ Th | 30,6 months | α | 5,99 | ²²² Ra |
| ²²⁷ Th | 18,7 days | α | 6,14 | ²²³ Ra |
| ²²⁸ Th | 1,9 years | α | 5,52 | ²²⁴ Ra |
| ²²⁹ Th | 7340 years | α | 5,17 | ²²⁵ Ra |
| ²³⁰ Th | 75380 years | α | 4,78 | ²²⁶ Ra |
| ²³¹ Th | 25,5 hours | β^- | 0,39 | ²³¹ Pa |
| ²³² Th | $1,4 \times 10^{10}$ years | α | 4,08 | ²²⁸ Ra |
| ²³³ Th | 22,3 months | β^- | 1,24 | ²³³ Pa |
| ²³⁴ Th | 24,1 days | β^- | 0,27 | ²³⁴ Pa |

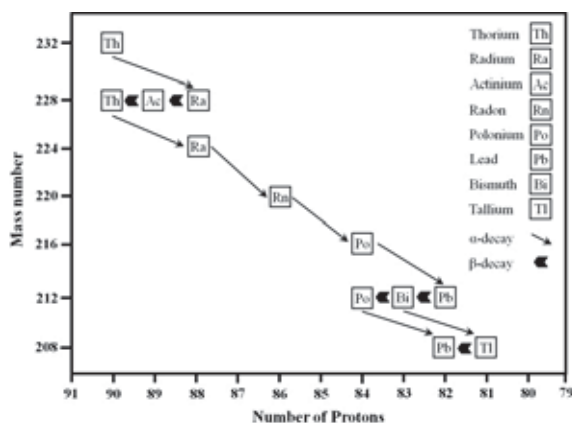


FIGURE 1
Thorium decay chain.

chemical toxicity compared with uranium, it can be considered dangerous for inhalation or massive ingestion because of its α emission, increasing the risk of lung cancer and leukemia (as example an Effective Dose of 1 Sievert can be reached with the inhalation of 2,22 gr of elemental thorium). This danger exists above all for people who work in an industry that mines [12], mills, or manufactures products containing thorium [13], such as ceramic glazes and lantern mantles [14]. Thorium presents a moderate tendency to bioaccumulation that could increase the risk related to the exposure to this element [15, 16].

Various analytical techniques have been successfully applied to determine thorium concentrations in different environmental samples but inductively coupled plasma mass spectrometry (ICP-MS) has both high sensitivity and good accuracy of isotope measurements, together with a relatively easy samples preparation procedure [17, 18, 19, 20]. Besides this technique, use of Inductively Coupled Plasma/Optical Emission Spectrometry (ICP-OES) is also possible, due to the presence of thorium essentially in one isotopic

form, as above-mentioned. However, such technique shows a sensitivity almost three order of magnitude minor [21] than ICP-MS.

Atomic Absorbance Spectrometry (AAS) is another technology suitable for analysis of metals in environmental matrix. However, the difficulty in finding of the hollow-cathode lamp, essential to perform this kind of analysis, makes such technique little used. These are the reasons that make this technique a reference method for the determination of long-lived radionuclides in environmental samples.

Other analytical techniques, such as laser ablation, which are able to directly analyze solid samples [22, 23] also in complex as sediment [24] are available, but to obtain reliable results a particular sample preparation consisting in pellets preparation is required.

The only other techniques that have found some use for the quantification of this element in environmental matrices are the radiometric ones, especially the alpha spectrometry [25], and gamma spectrometry [26, 27]. These techniques have the advantage to directly quantify the radioactivity emitted, which is undoubtedly the most important unknown factor as regards environmental issues and work safety, and unlike ICP-MS no samples preparation is required. By contrast, due to the low thorium activity, they are less sensitive than the technique of reference, at least at standard concentrations for sample of environmental interest. In particular, for the determination of long-lived radionuclides, ICP-MS offers lower limits of detection (LOD) than those provided by radiometric techniques (e.g. α -, β -spectrometry). However, frequently nowadays ICP-MS and radiometric techniques are used together to quantify radioactive trace elements as thorium especially in environmental [28] or complex samples [29] in

order to have a completely independent analytical method to confirm the results.

One other small but important niche in applications of radiometric techniques is related to the development of portable devices used to carry out mainly radionuclides detection [30] in situations concerning homeland security or mass disaster. In this crucial field, a complex set of tools has been developed to protect critical infrastructures [31, 32, 33], to simulate attack's effects [34, 35], and to study real case already occurred [36].

Hand-held tools developed in this sector, especially those of recent production, may show considerable analytical performances and find useful application even in a context demanding in terms of performance as the environment. For example, portable instruments based on Ion Mobility Spectroscopy (IMS), and born for chemical weapons analysis, could be used for the screening of samples as well as for the analysis of volatile substances in soil [37, 38].

In our work we want to evaluate the possibility to use the analytical performances offered by a portable gamma spectrometer as a ICP-MS confirmatory technique even on a difficult analyte such as thorium in concentrations of the order of mg/kg. We will use as reference material soil from a firing range and as blank unpolluted soil sampled outside the site.

EXPERIMENTAL

Chemical Analysis - Induced Coupled Plasma - Mass Spectrometry. Sampling. Small quantities of soil (on the order of grams) were taken with a manual auger. The instrument excludes the material larger than 2 cm.

Sample preparation. Before the analysis, further dimensional exclusion was carried out through a vibratory sieve shaker (AS200, Retsch) after drying, and leaving for the analysis only the material with a particle size minor than 2 mm. It proceeds, then, to chopped samples with mixer mill (MM 200, Retsch) in order to reduce final fineness (range 5-10 μm) prior to start with instrumental analysis. After the homogenization process, aliquots of soil (~0,3 g) were placed in Teflon containers and 10 mL of ultrapure HNO_3 (67,9%, Fluka) was added to mineralize the sample, allowing the passage of all ions in solution. Then the samples were placed in a microwave oven (Milestone Ethos)

and a cycle of mineralization was performed, maintaining for 10 minutes at 1000 W up to progressive increase of 180°C, then keeping for an additional 10 minutes at 1000 W at fixed temperature to 180°C. After cooling, the samples were filtered and diluted 1:14 in water solution of HNO_3 (1% v/v).

Data analysis. To carry out the analytical procedure, an Induced Coupled Plasma - Mass Spectrometer XSeries II (Thermo Electron) was used. The instrument was connected to an autosampler ASX-520 (CETAC). For quantitative analysis, solutions with known and certificates standards were prepared (concentration standard solutions: 1000 $\mu\text{g/L}$, 500 $\mu\text{g/L}$, 100 $\mu\text{g/L}$ and 50 $\mu\text{g/L}$ [ppb]) and calibration lines were performed. Data were processed with the help of the software Plasmalab. To evaluate the element variability in the matrix, 6 replicates were performed for each sampling point.

Physical Analysis – Gamma Spectrometry. Sampling. One kilogram a relatively large amounts of soil were taken by simple spoons. Samples were placed in large plastic containers, in which could also be done later analysis.

Sample preparation. In contrast to the relatively elaborate procedures for chemical analysis, physical analysis samples undergo only air drying procedures within a standard laboratory oven. Samples were analyzed both externally and internally to the glass containers with which they were taken, in order to limit the errors due to sample handling.

Data analysis. To perform the analytical procedure, a support system by ITECO and a Gamma Spectrometer based on a high purity germanium detector Detective EX100 by ORTEC cooled with a stirling cooler have been used (Figure 2). For the spectra acquisition the software of qualitative and quantitative analysis by gamma spectrometry (GammaVision-32, ORTEC) was used. The information returned by the detector depends on the number of the generated charge by the incident radiation in the detector. Spectra were continuously acquired for 72 h in the range among 0 and 3000 KeV. The spectroscopy measurement follows a Poissonian counting statistics, and the error is proportional to the root of the number of counts according to the Eq. (1):

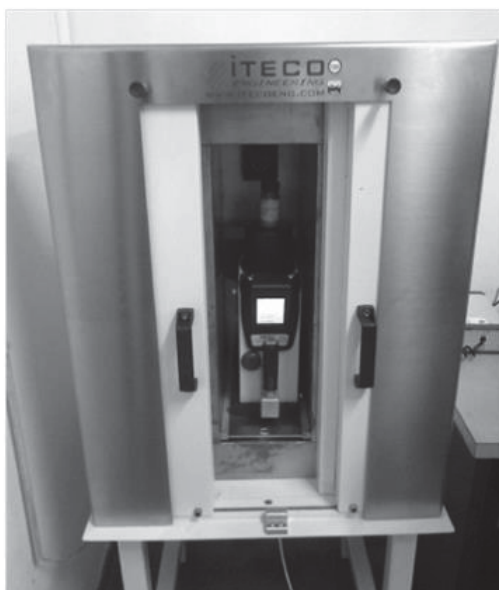


FIGURE 2
Support system and gamma spectrometer.

$$\sigma = K \times \sqrt{N} \quad (1)$$

where: σ represents the standard deviation, K represents the proportionality constant, N represents the tests number.

Quantitative measures for thorium was performed using the following approach. By using specific activities reported in literature and applying appropriate calculus equations it is possible to convert concentrations in activity and vice versa. To perform calculations, specific activity must be transformed in mass using the values calculated in literature. In our case, we have to consider that the first radioactive isotope in secular equilibrium with ^{232}Th is ^{228}Ra , which is in turn in secular equilibrium with ^{228}Ac that has a very short life period. For this latter isotope it is possible to measure the activity, that coincides with that of ^{228}Ra owing to the secular equilibrium. In literature, its specific activity amounts to 4,054 kBq/g. For the reason already mentioned, the same value can be considered for ^{232}Th . ^{228}Ac activity was measured starting from photopeaks of 911,21 keV and 968,97 keV energy (Figure 3).

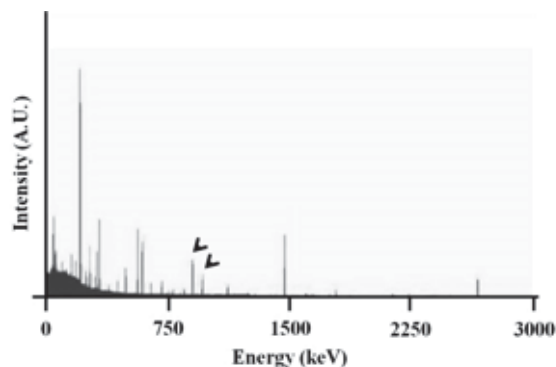


FIGURE 3
 γ spectrum for a sample of soil. The intensity of the signal is shown in logarithmic scale. The displayed peaks were compared by libraries. Arrow heads shown the activity of ^{228}Ac (photopeaks of 911,21 keV and 968,97 keV). The spectrum was acquired for 72 hours in the range between 0 and 3000 keV. A.U. = arbitrary units.

RESULTS AND DISCUSSION

Both approaches used in the present work return values in good agreement with each other (Table 2), nevertheless each method exhibit advantages and disadvantages.

As expected, ICP-MS technique is definitely more sensitive: due to the very low background noise, it is able to identify ions in very low concentrations, even lower than the parts per billion (ppb). This technique allows to quantify isotopes present in traces and allows to calculate the isotopic ratio in a simple way, by calculating the ratio between the peaks areas. However, ICP-MS technique allows to analyze only liquid samples and then is necessary a pre-treatment step of acid mineralization, that increases the uncertainty. In fact, in a proper error analysis, the uncertainty due to the weight of sample dilution and possible non-complete dissolution of the sample it should be added and however ICP-MS, as in most chemical methods of analysis, the

TABLE 2
ICP-MS and γ spectrometry results.

| Sampling sites | ICP-MS (mg/Kg) | Sample activity (Bq) | γ spectrometry (mg/Kg) |
|----------------|----------------|----------------------|-------------------------------|
| Blank | 4,6 \pm 0,4 | 21,8 | 5,4 |
| Area 1 | 14,6 \pm 1,2 | 72,4 | 17,9 |
| Area 2 | 8,9 \pm 0,6 | 40,5 | 10,0 |
| Area 3 | 10,1 \pm 2,0 | 48,0 | 11,9 |



concentration of heavy metals in solution must be calculated, not directly the activity or gamma radiation emitted. As previously reported, gamma spectrometry returns a direct measurement of radioactivity. The activity can be converted in concentration using the values of specific activity, but in this way the measure becomes indirect and introduces a margin of error and uncertainty due to factors that could affect the radiation emitted, such as co-presence of multiple isotopes gamma emitters, crossed matter, matrix effect, etc.

CONCLUSIONS

Our work demonstrates that, under certain conditions, it is possible to use a portable device also for quantitative analysis, being able to perform control measures with an analytical techniques, independent from ICP-MS technologies, even if some limitation should be accepted, for example the long duration of measurements. The quality of this result could be improved using a low background shield, in order to reduce the noise from environmental background and that due to cosmic rays, and especially because correction systems, such as the calculation of the sample self-absorption, were not applied. More accurate calculations that consider the self-adsorption would be possible only after a chemical soils analysis. These first experimental data show that these corrections are not essential. This work would also be an encouragement to a better management of this kind of instrument that are frequently used only for screening purpose and that instead, especially in newer models, have significant performance.

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