

GAMMA SPECTROMETRY IN THE DETERMINATION OF RADIONUCLIDES COMPRISED IN RADIOACTIVE SERIES

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ABSTRACT

Gamma spectrometry is an analytical technique extensively employed in radionuclide determination. The usual ease of sampling preparation, the wide range of natural and artificial radionuclides that can be determined, and the applicability of this technique in a variety of sample matrices are some of its advantages. However, some care is needed when the technique is intended to be used as a tool for identification and quantification of radionuclides comprised in radioactive decay series. In such situations, as the radioactivity contents in the sample can naturally vary along the time, the results are critically dependent of the radioactive equilibrium conditions of the sample. In this work, we outline some criteria to decide about the radionuclide equilibrium situation expected to occur in various kinds of samples and thus decide the procedure to be taken to assure the reliability of the results in such complex situations. Provided that such analysis is carried out, gamma spectrometry can be used even in the determination of radionuclides that do not directly emit gamma radiation, based on the concentration of their gamma-emitter decay products. Different procedures, especially related to the delay time and sample sealing to assure proper radioactive equilibrium conditions, are required prior to the sample measurement, according to the origin and composition of the analyzed materials.

1. INTRODUCTION

Gamma spectrometry is an analytical technique extensively employed in radionuclide determination, due to the advantages of the usual ease of sampling preparation, the wide range of natural and artificial radionuclides that can be determined, and the applicability of this technique to a wide variety of sample matrices.

However, some care is needed when the technique is intended to be used as a tool for identification and quantification of radionuclides comprised in radioactive decay series.

In this work, we outline some criteria to decide about the radionuclide equilibrium situation expected to occur in various kinds of samples and thus decide the procedure to be taken to assure the reliability of the results in such complex situations. Provided that such analysis is carried out, gamma spectrometry can be used even in the determination of radionuclides that do not directly emit gamma radiation, based on the concentration of their gamma-emitter decay products.

2. TRANSIENT AND SECULAR EQUILIBRIUM CONSTRAINTS

The secular equilibrium over the entire radioactive series can be assured in essentially one situation, that is, in solid rocks that have not been submitted to geochemical partitioning. For samples from other origins, for instance generated from industrial processes, as the radioactivity contents in the sample can naturally vary along the time, the results are critically dependent of the radioactive equilibrium conditions of the sample [1].

For analytical purposes, a common and effective practice is the sealing of a sample to obtain transient equilibrium. The time interval is usually set to 10 times the half-life of the intermediate radionuclide with the longest half-life. The sealing is necessary to avoid the escape of Radon, which could break the equilibrium.

3. DETECTION EFFICIENCY

Activity determination by gamma spectrometry, in its simplest form and without respect to several corrections related to radioactive decay, coincident countings [2] and gamma-ray attenuation, is evaluated by using the well-known expression

$$A = \frac{C}{\epsilon_{\gamma} \cdot I_{\gamma} \cdot t_L} \quad (1)$$

where A is the activity (Bq), C is the countings net area, ϵ_{γ} is the efficiency corresponding to the energy of gamma line γ , I_{γ} stands for the emission probability, also known as the line intensity, and t_L is the live counting time.

From this expression, one can observe that efficiency and intensity for each gamma line play the major role in the expected *a priori* detection limit. The actual detection limit is also dependent of each particular sample radioactive content, which affects the spectrum base line. These issues should be taken in account when one is choosing the gamma lines to perform an analysis in a particular counting system.

4. PARTICULAR ISSUES FOR SOME PRECURSOR RADIONUCLIDES

Depending on the target radionuclide, the criteria adopted to guide the analysis are described as follows.

4.1. Detection of Uranium

Natural Uranium is composed by 3 isotopes, ^{234}U , ^{235}U and ^{238}U [3]. ^{235}U is a gamma emitter with 4 main lines easily identified in a gamma spectrum. The strongest of them, however, is very close to the 185 keV line from ^{226}Ra . Nonetheless, the remaining lines, at 143.76, 163.33 and 205.31 keV, are relatively free from interferences and can be used in gamma spectrometry.

The use of ^{235}U to extrapolate total Uranium is acceptable only when one can assure that the natural abundance is preserved. In this case, however, the detection limit is usually high, due to the low abundance of ^{235}U in natural Uranium, namely 0.72%.

In some situations, Uranium can be detected by measuring ^{234}Th , the immediate descendant of ^{238}U . It should be noted, however, that as ^{234}Th has a half-life of 24.1 days, if one are dealing with samples where Uranium and Thorium were chemically separated, which is a common situation in processes of the nuclear fuel cycle, a sample containing U will reach transient equilibrium with ^{234}Th only after about 8 months after the separation.

In such cases, the ^{234}Th 63.290 keV line is commonly used, because it is relatively free of interferences from X-ray lines [4]. This is not the case for the 93 keV line – actually a doublet –, often affected by fluorescence X-ray interferences.

Another possibility, and when one can assure that the sample is in transient equilibrium, is the use of the weak gamma lines from $^{234\text{m}}\text{Pa}$, at 766 and 1001 keV [5]; however, they are present only in quite concentrated and old Uranium samples.

The detection limits for ^{238}U in such situations is an important issue. Usually, ^{238}U determination can be performed with alpha spectrometry or, when available, neutron activation analysis (NAA), both with much lower detection limits. However, when neutron sources for NAA are not readily available, or when the time consuming sample preparation and measuring, characteristics of alpha spectrometry, are not acceptable for routine analysis, gamma spectrometry can be an interesting option.

4.2. Detection of ^{226}Ra

The radionuclide ^{226}Ra , although pertaining to Uranium series, due to its long 1600 years-half-life is considered as a precursor of its own subseries, comprising the gamma-emitters radionuclides ^{214}Pb and ^{214}Bi . The next long-lived nuclide is ^{210}Pb , thus breaking again the Uranium series.

Determination of ^{226}Ra is usually performed following a minimum 38 days delay after sample sealing, corresponding to 10 half-lives needed to allow for the growing of ^{222}Rn progeny. ^{226}Ra itself has a gamma-ray at 185 keV, but it coincides with a gamma line from ^{235}U and for this reason this line is not commonly used to quantify ^{226}Ra .

Once equilibrium is obtained, ^{226}Ra quantification is made by its descendants. Table 1 presents the relevant gamma lines in this case.

Table 1. Relevant gamma lines in ^{226}Ra detection

Actual emitter	Energy (keV)	Intensity (%)
^{214}Pb	351.9	35.8
^{214}Bi	609.3	44.8

4.3. Detection of Thorium-232 and Radium-228

Determination of ^{232}Th by measuring the strong gamma lines from ^{228}Ac has been reported. However, as in the case of U determination, equilibrium situation must be evaluated. While such secular equilibrium can be guaranteed in solid samples like rocks that did not suffered weathering, this is not necessarily the case for soil samples or, generally, for weathered or processed samples. In soil, geochemical processes can separate Th and Ra, thus carrying out the ^{228}Ra isotope, which is immediately before ^{228}Ac in the decay chain.

By its turn, ^{228}Ra , with a 5.7 y half-life, is easily detected by some of the several lines of its short-lived descendant, ^{228}Ac , the most useful presented in Table 2. The 964.8 and 968.9 keV lines, although intense, are omitted, because they are close enough to demand separation with mathematical fitting procedures, which rises the uncertainty in the result.

Table 2. Main gamma lines of ^{228}Ac

Energy (keV)	Intensity (%)
911.2	35.8
338.3	44.8

4.4. Detection of ^{228}Th in Equilibrium with ^{224}Ra

Following the Thorium series, the next long-lived radionuclide after ^{228}Ra is ^{228}Th , an alpha emitter having a 1.9 y half-life. As ^{228}Th decays through a series of short-lived nuclides until the stable ^{208}Pb , the various gamma lines from ^{212}Pb , ^{212}Bi and ^{208}Tl can be used to evaluate ^{228}Th , provided a 36 days delay after sample sealing is adopted, to allow for the growing of ^{224}Ra , which has the longest half-life among the short-lived nuclides in the series. The sealing is needed because a Radon isotope, ^{220}Rn , is present in the series.

The strong 238.6 keV line from ^{212}Pb should be avoided for quantification, as it is near the 241 keV line from ^{224}Ra . One should also note that when using the lines from ^{208}Tl to be aware of the branching ratio in the ^{212}Bi decay, which causes the ^{208}Tl activity to be 36.2 % of that of ^{228}Th .

4.5. Detection of ^{210}Pb

Since HPGe detectors with high energy resolution, low background and thin Be windows designed to minimize gamma attenuation became available, ^{210}Pb detection has been extensively performed by measuring of its 46 keV gamma line.

Such a low energy poses additional challenges in the detection, especially with extended and dense samples. Gammas in this energy range are easily self-attenuated by the sample, so the activity quantification is limited to samples in counting geometries as thin fiber filters, for which self-attenuation can be neglected, or diluted aqueous solutions, for which it can be evaluated using ^{210}Pb standard sources placed on the sample [6]. Thus, for any other kind of matrix - soils, powders, etc. - the sample must be chemically pre-treated in order to obtain a homogeneous aqueous solution suitable for the measurement.

On the other hand, there are no need to concerns about radioactive equilibrium, due to the long ^{210}Pb half-life of about 22 years, and for the gamma is emitted by ^{210}Pb itself and not by descendant nuclides.

5. CONCLUSIONS

We can conclude that several issues, depending on the origin of the samples, whether if it is from natural origin, like a pulverized rocks or it is manmade, like an industrial byproduct or an artificial radiation source. Different procedures, especially related to the delay time and sample sealing to assure proper radioactive equilibrium conditions, are required prior to the sample measurement, according to the origin and composition of the analyzed materials.

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