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ORIGINAL

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Determination of potassium and sodium in an ash sample by gamma-ray spectroscopy

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Abstract Neutron activation analysis and gamma-ray spectroscopy were used to determine the quantity of potassium and sodium in an ash sample of *Tabebuia* sp bombarded with thermal neutrons. These techniques, widely applied in nuclear physics, can be used in the context of wood science as an alternative for the usual physical chemistry methods applied in this area. The quantity of K and Na in an 8.60 ± 0.10 mg of ash was determined as being 1.3 ± 0.3 mg and 11.0 ± 1.8 μg, respectively. The ratio of *Tabebuia* sp converted into ash was also determined as $0.758 \pm 0.004\%$.

Introduction

The determination of chemical elements in wood samples is crucial in various experiments (Andrade and Mattiazo 2000; Cutter and Murphey 1978; Guedes and Poggiani 2003; Humar et al. 2004; Ismael et al. 1998; Morell and Huffman 2004; Paiva et al. 2002). The greatest part of these experiments uses some physical chemistry method (Fengel and Wegener 1984) to measure the elements of interest (Humar et al. 2004; Morell and Huffman 2004) with no mention of the uncertainties involved in the process.

Radioactive methods are widely used in the context of physics and they are spreading out to some interdisciplinary fields like, e.g., biology (Arruda-Neto et al. 2001). One of these methods is gamma-ray spectroscopy which is used to measure the gamma-rays emitted by radioactive nuclides. These nuclides can be produced exposing, for example, a wood sample to neutrons. Neutrons penetrate the nuclei, producing radioactive isotopes. Each isotope then decays with

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the emission of gamma radiation with energy and intensity characteristic for the isotope. Gamma-ray spectroscopy is used to identify and quantify the isotopes in the sample. This technique has already been used in wood science (Meyer and Siau 1976; Unlu et al. 2005) but without a careful description of the experimental procedure.

In this paper, we propose the use of gamma-ray spectroscopy as an alternative and powerful method to determine the quantity of potassium and sodium in a *Tabebuia* sp ash sample. The *Tabebuia* sp or ipê is a typical Brazilian tree. Its species (*Tabebuia serratifolia*, *T. chrysotricha*, *T. roseo-alba*, etc.) present not only economic and ornamental values, but also play a vital role in reforestation programs. The tree's elementary components, in particular the minerals, are of great importance to its growth. The quantities of these minerals vary, for example, according to species, soil conditions and individual growth requirements. Our decision to determine the sodium and potassium content was based on their abundance in the ash, and their importance to the growth of the tree.

In this paper, we will give a detailed description of the experimental method showing that various elements can be determined using this technique, and present results for a sample of *Tabebuia* sp. We also measured the ratio of *Tabebuia* sp converted into ash. The paper is organized as follows. In Sect. 2, we give the experimental method used in this work and explain how to quantify the elements. In Sect. 3, we present our numerical results. Our conclusions are summarized in Sect. 4.

Experimental

Sawdust from the stem (~1 m above the soil) of an urban *Tabebuia* sp was incinerated at 600°C in a mufla furnace to produce 8.6 ± 0.10 mg of ash. This ash sample was irradiated with neutrons in the nuclear reactor at Instituto de Pesquisas Energéticas e Nucleares (IPEN—Brazil) with a flux of $\phi = 1.5\times10^{13}$ n cm^{-2} s^{-1}, where n represents a neutron. The thermal neutrons (low energy) in the reactor penetrate the potassium and sodium nuclei and the following nuclear reactions occur (these reactions were used to study the quantity of Na and K): $^{23}\mathrm{Na} + \mathrm{n} \rightarrow {}^{24}\mathrm{Na} + \gamma$ and $^{41}\mathrm{K} + \mathrm{n} \rightarrow {}^{42}\mathrm{K} + \gamma$, γ is a gamma-ray. [In other notations, these reactions can be represented as ^{23}Na(n, γ)^{24}Na and ^{41}K(n, γ)^{42}K.]

The nuclides ^{24}Na and ^{42}K are unstable and emit, respectively, the characteristic gamma energies, E_γ, of 1368.598 ± 0.006 and 1524.58 ± 0.08 keV that can be detected by a high-purity germanium detector (HPGe).

The number of nuclides presented on the left-hand side of the nuclear reactions shown in the first paragraph of this section is given by:

$$N = \frac{A}{I\varepsilon} \frac{\mathrm{e}^{\lambda t}}{1 - \mathrm{e}^{\lambda \Delta t}} \frac{1}{\sigma \phi \; t_i} \tag{1}$$

In Eq. 1 N is the number of ^{23}Na or ^{41}K. Hundred percent of the sodium in nature is the isotope ^{23}Na. For potassium, about 93.26% is ^{39}K and 6.73% appears as ^{41}K. A is the peak area located at ^{24}Na and ^{42}K respective energies. I is the intensity of the gamma line. ϵ is the detector efficiency (it is a function of the energy and the distance from the radioactive source to the detector). $\lambda = \ln(2)/t_{1/2}$, where $t_{1/2}$ is the nuclide half-life (the time necessary for half of

the nuclei to decay). t is the time interval from the end of the irradiation and the begin of the measurements. Δt and t_i are the measurement and irradiation time, respectively. The factor σ is the thermal neutron cross section, which can be understood as the relative probability for the reaction to occur.

The ratio of the *Tabebuia* sp transformed into ash was calculated from three measurements. The sawdust was placed in an oven at 100°C for approximately 2 days in order to carefully dry the sample. It was then weighed and placed in a muffle furnace at 600°C. The resulting ash was weighed and the ratio of the mass of the ash to the mass of the oven-dried wood was calculated.

The variances, s^2, were calculated in the usual manner. If y (x_1, x_2, x_3,...) is a function of the physical quantities x_i ($i = 1,2,3,...$) each one with the respective standard deviation s_i, then the y variance is given by

$$s_y^2 = \left(\frac{\partial y}{\partial x_1}\right)^2 s_1^2 + \left(\frac{\partial y}{\partial x_2}\right)^2 s_2^2 + \left(\frac{\partial y}{\partial x_3}\right)^2 s_3^2 + \cdots = \sum_i \left(\frac{\partial y}{\partial x_i}\right)^2 s_i^2 \quad (2)$$

where $s^2{}_y$ is the variance associated with the quantity y and $(\partial y/\partial x_i)^2$ is the partial derivative of y with respect to x_i.

Results

Figure 1 shows the full spectrum of the irradiated ash. The horizontal and vertical axes are the gamma energy in keV and the number of counts in each

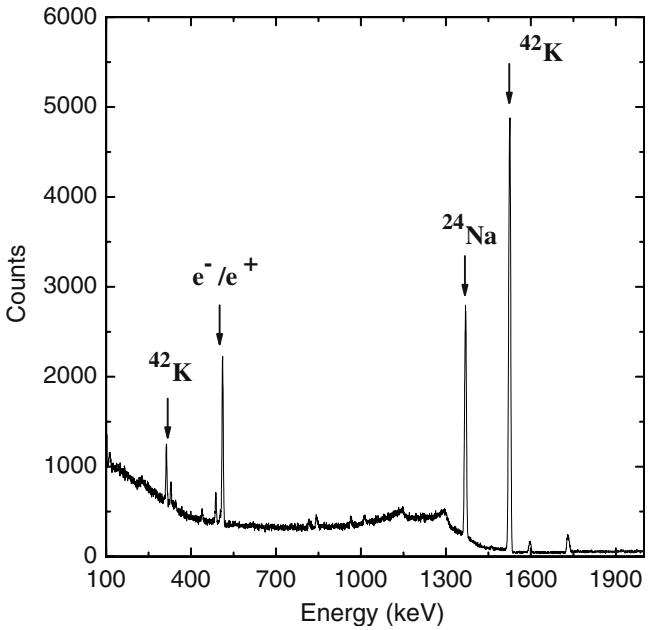

Fig. 1 Full spectrum of the irradiated ash. The *arrows* point to the relevant peaks in the analysis of ^{42}K and ^{24}Na. The 511 keV peak refers to the electron (e^-) positron (e^+) annihilation

channel (energy interval), respectively. The arrows show the main peaks related to the nuclides of interest ^{42}K and ^{24}Na. The peak at 511 keV refers to the electron (e^-) positron (e^+) annihilation. The other minor peaks refer to elements that are beyond the scope of this paper.

Figures 2 and 3 show the regions around the peaks for ^{24}Na at 1368.598 ± 0.006 keV and ^{42}K at 1524.58 ± 0.08 keV. A function (Gaussian + offset + exponential) was fitted to both peaks using the method of minimum squares. Tables 1 and 2 list the parameters for the irradiation and the physical characteristics of each nuclide.

The number of ^{23}Na and ^{41}K in the ash sample calculated from the data presented in Tables 1 and 2 is

$$N_{^{23}\mathrm{Na}} = \quad 2.9 \pm 0.5 \times 10^{17}$$
$$N_{^{42}\mathrm{K}} = \quad 1.3 \pm 0.3 \times 10^{18}.$$

The standard deviations were calculated using Eq. 2 from the uncertainties presented in Tables 1 and 2. The physical quantities with no indicated uncertainty were considered with a non-significant error.

Remembering the abundance of ^{23}Na, 100%, and ^{41}K, 6.73%, we can calculate the total mass of sodium, M_{Na}, and potassium, M_K, in the ash sample:

$$M_{\mathrm{Na}} = \quad 11.0 \pm 1.8 \ \mu \mathrm{g}$$
$$M_{\mathrm{K}} = \quad 1.3 \pm 0.3 \ \mathrm{mg}.$$

The ratio of *Tabebuia* sp transformed into ash, $0.758 \pm 0.004\%$, was obtained from three measurements as explained at the end of Sect. 2.

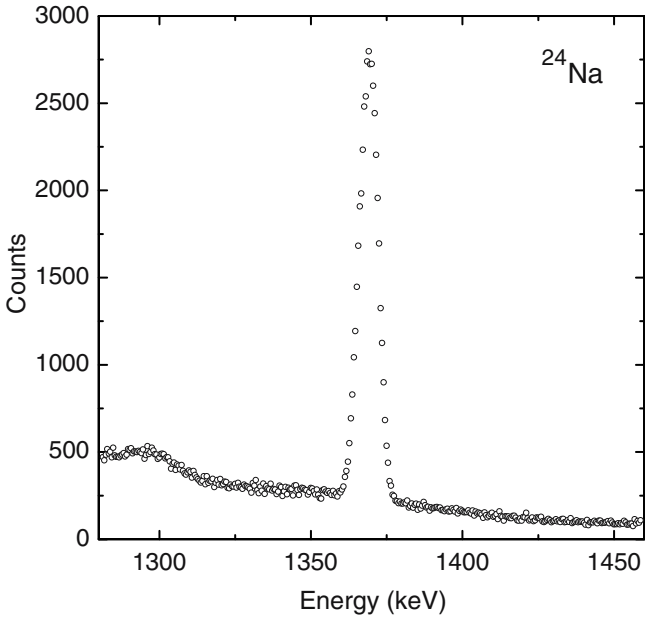

Fig. 2 Region of 1,368 keV showing the ^{24}Na peak. The *open circles* are the counts in each channel (energy)

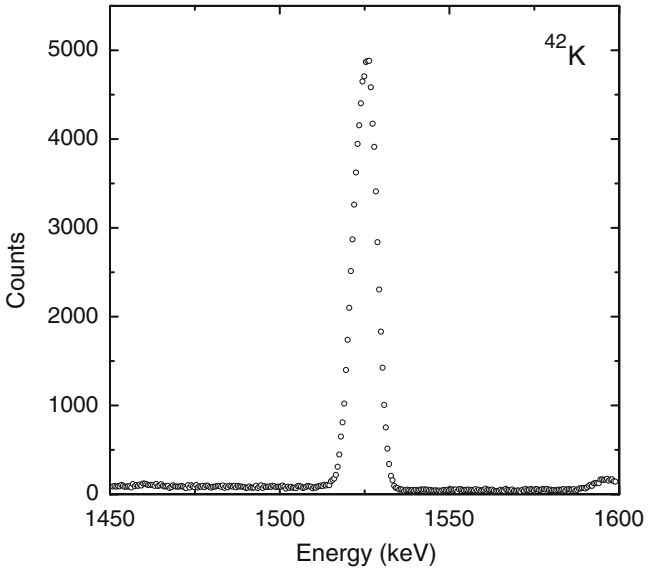

Fig. 3 Region of 1,524 keV showing the ^{42}K peak. The convention of the *symbols* is the same as given in Fig. 2

Conclusions

In the present work, we measured the quantity of potassium and sodium in an ash sample of 8.4 mg and the ratio of *Tabebuia* sp transformed into ash. The obtained results, order of microns for sodium, show the sensitivity of our method which, in special cases, can detect the presence of ppb of elements in the samples. We can use this method with a few modifications (we may irradiate the sample with protons) to determine other elements not only in the ash but in other samples to quantify, for example, the heavy metals coming from sewage sludge (biosolids) in a soil sample (Andrade and Mattiazo 2000). Table 3 shows some elements that can be determined by gamma-ray spectroscopy.

We can see from Table 3 that the nuclear technique used in this paper, and widely used in physics, is a very powerful method to determine the quantity of elements in any sample and can make precious contributions in other areas such as wood science.

Table 1 Irradiation parameters

Parameters	
t_i	0.083 h
t	63.17 h
Δt	1 h
ϕ	5.4×10^{16} n cm^{-2} h^{-1}

t_i is the irradiation time, t is the time interval from the end of the irradiation to the beginning of the measurements. Δt is the irradiation time and ϕ is the neutron flux in the IPEN's nuclear reactor

Table 2 Physical characteristics of ^{24}Na and ^{42}K

Parameters	^{24}Na	^{42}K
$t_{1/2}$	14.659 ± 0.004 h	12.360 ± 0.003 h
E_γ	1368.598 ± 0.006 keV	1524.58 ± 0.08 keV
I	100%	18.8%
ϵ	0.033 ± 0.005	0.033 ± 0.005
A	15210 ± 210	59500 ± 300
Reaction	^{23}Na(n, γ)^{24}Na	^{41}K(n, γ)^{42}K
σ	0.40 ± 0.03 b	1.46 ± 0.03 b

$t_{1/2}$ is the nuclide half-life (the time necessary for half of the nuclei to decay), E_γ is the characteristic gamma energy, I is the intensity of each gamma line, ϵ is the detector efficiency, A is the peak area (at ^{24}Na and ^{42}K energies, see Figs. 1, 2, 3), reaction is the nuclear reactions that form ^{24}Na and ^{42}K and σ their cross sections in barns (b) ($1b = 10^{-24}$ cm^2)

Table 3 Examples of elements that could be determined by gamma-ray spectroscopy

Element	Reaction	$t_{1/2}$
K	^{41}K(n,γ)^{42}K	12 h
Na	^{23}Na(n,γ)^{24}Na	15 h
N	^{14}N(p,2α)^{7}Be	53 days
Cr	^{52}Cr(p,n)^{52}Mn	5 days
Cu	^{63}Cu(p,2n)^{62}Zn	9 h
	^{65}Cu(p,n)^{65}Zn	244 days
Ni	^{58}Ni(p,pn)^{57}Ni	35 h
Zn	^{64}Zn(p,p2n)^{62}Zn	9 h
	^{66}Zn(p,pn)^{65}Zn	244 days

The first column is the element to be determined in the sample, the second and third columns indicate the nuclear reactions that may occur, and the corresponding half-lives of the radioactive products. p is a proton and γ a gamma-ray. α is a ^{4}He nucleus

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