$^{40}$K, $^{137}$Cs and $^{232}$Th activities in Brazilian milk samples measured by gamma ray spectrometry

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This work deals with the measurement of radioactivity in powdered milk, with high-resolution gamma-ray spectrometry, using a HPGe detector. Preliminary measurements were accomplished to define the kind of the system shield, the geometry of the sample recipient, the size of the sampling and the self-absorption correction. It was possible to measure the radionuclides $^{40}$K, $^{137}$Cs and $^{232}$Th. Tukey’s average comparison test was used to check the repeatability of the measurements.

1 Introduction

The measurement of radioactive elements in the environment and in foodstuffs is of fundamental importance for controlling the radiation levels to which man is exposed directly or indirectly. Due to the dozens of nuclear weapons tests and several nuclear reactor accidents, various artificial radioactive elements were introduced in the biosphere, besides natural radionuclides. Another important fact is that, in the case of a nuclear accident anywhere in the world, through the importation of contaminated foods, the health of people of any region can be indirectly affected.

The main sources of radionuclides in alimentary diet are milk, meat and other products more frequently consumed. Among them, milk is the most studied because it is a basic constituent of the diet of the children, and they are more sensitive to radiation because their organism is in growing phase.

The literature about $^{137}$Cs and other radionuclides in foodstuffs of countries in the northern hemisphere is quite abundant. However in southern hemisphere, especially in Latin America, availability of this kind of information is poor. In Brazil, quantitative data about natural radioactivity exist only for south-west region of the country, mainly Rio de Janeiro state. Brazil is a continental country, with varied mineralogy and geology that makes studies necessary in many states of the federation. Londrina is located in the southern region of Brazil and has a University with the equipment necessary to develop this kind of study.

The purpose of this work is to identify and quantify radio nuclides in powdered milk samples produced in Londrina city, Paraná state region, located in the south of the country.

Materials and Methods

Two different trademarks of powdered milk, produced in Londrina region, were analyzed by high-resolution gamma-ray spectrometry. A coaxial HPGe detector with 10% relative efficiency coupled with a standard nuclear electronics and a 8 K multi-channel card was used. The measured total energy resolution was 1.95 keV for the line of 1408.12 keV and 1.39 keV for the line of 344.28 keV, both from $^{152}$Eu.

The number of samples used to estimate sample population parameters was magnified by a procedure that involves statistical inference. This is essential, because to take a large number of samples can be a waste in relation to the cost, time, work, etc. On the other hand, a small number of samples may provide an unreliable result, due to a large statistical fluctuation. In the present work the determination of the sampling size was calculated from the confidence level components, given by

$$n = \frac{Z^2 \cdot \sigma^2}{d^2}$$

...(1)
where \( n \) is the number of samples, \( d \) is the estmative variation amount in relation to the population true value, \( Z \) is the confidence coefficient and \( \sigma \) is the standard deviation.

To obtain the ideal value of \( n \) the data of \(^{40}\text{K}\) concentration in Venezuelan milk\(^2\) was used. The corresponding data for Brazilian milk found in the literature (and reported in the results) did not present the deviation for the measured concentration level and could not be used in Eq. (1). It was found that the number of samples must be between 3 and 15. For each lot of milk, six samples were taken for measurements of \(^{40}\text{K}\) concentration, providing a confidence level of 95%.

The two milk brands analyzed, Integral Powdered Milk Cativa and Integral Powdered Milk Polly, were put in 2.1 liter Marinelli beakers with net mass varying between 1100 and 1500 g, although most of them were between 1130 and 1230 g. Table I presents the main sample characteristics. Three measurements spread over two days (172800s) were done for each sample and for the background. Measurement using \(^{152}\text{Eu}\) source was used for 24 h (86400 s) to monitor the system calibration. The best shielding arrangement for the energy region of interest was a sequence of lead, iron and aluminium. The experimental and electronic set up is shown in Fig. 1.

The samples were analyzed using gamma-ray spectrometry and the calibration factor, obtained from Eq. (3), was calculated for the main gamma-ray lines in the spectrum. The activity was calculated according to the IAEA norms\(^3\).

The activity of a radionuclide can be calculated considering the following factors, according to the equation

\[
A = \frac{N_L}{\varepsilon P_{\gamma} m t} \tag{2}
\]

where \( A \) is the sample activity concentration in Bq/kg, \( N_L \) is the net number of counts measured under the peak, \( \varepsilon \) is the system detection efficiency (number < 1), \( P_{\gamma} \) is the absolute transition

![Fig. 1 — System geometry and sketch diagram of the experimental set-up](image)

Table I — Milk samples characteristics

<table>
<thead>
<tr>
<th>Milk</th>
<th>Density(^*) (g/cm(^3))</th>
<th>Nominal Moisture</th>
<th>Measured Moisture(^*)</th>
<th>Fabrication Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cativa</td>
<td>0.554 ± 0.002(^*)</td>
<td>2.8 - 3 %</td>
<td>4.7 ± 0.3(^*) %</td>
<td>30/08/1998</td>
</tr>
<tr>
<td>Polly</td>
<td>0.542 ± 0.007(^*)</td>
<td>3 %</td>
<td>5.2 ± 0.2(^*) %</td>
<td>14/08/1998</td>
</tr>
</tbody>
</table>

\(^*\)Mean value from the six prepared samples  
\(^*\)Mean Standard Deviation
The counts depend on the detection efficiency, which depends on the radiation amount that reaches the detector and its energy. This radiation amount depends on the absorption factor, the sample dimensions and density. These are the factors that determine the calibration parameter, which in this work will be written, for each gamma line, as

\[ \alpha = \frac{mAt}{N_L} \]  

... (3)

In order to obtain the \( \alpha \) values, samples with different known activities of several radionuclides were prepared. The calibrated samples were prepared using two IAEA soil samples, i.e., IAEA 375 and IAEA 326.

When a sample is introduced in a detector, the term related with the detection limit is the minimum detectable activity (MDA), expressed by

\[ MDA = \frac{\alpha N_{L\text{min}}}{m t} \]  

... (4)
\[ Y = A + B \cdot X \]

<table>
<thead>
<tr>
<th>Param</th>
<th>Value</th>
<th>sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.20724</td>
<td>0.1759</td>
</tr>
<tr>
<td>B</td>
<td>-1.05791</td>
<td>0.02707</td>
</tr>
</tbody>
</table>

\[ R = -0.99772 \]
\[ SD = 0.04729, N = 9 \]
\[ P = 1.871E-9 \]

![Graph](image)

**Fig. 3 — Counting efficiency versus energy**

**Table 4 — Measurements for \(^{137}\)Cs in natural milk**

<table>
<thead>
<tr>
<th>Present work</th>
<th>Diverse Values Activity(^a)</th>
<th>Biophysics Institute Activity(^a) (Bq/L)</th>
<th>Farnas Activity(^b) (Bq/L)</th>
<th>CNAAA Activity(^b) (Bq/L)</th>
<th>INB Activity(^b) (Bq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.82 - 1.32(^a)</td>
<td>0.23 ± 0.04</td>
<td>0.26 ± 0.08</td>
<td>0.14 ± 0.17</td>
<td>0.42</td>
<td>0.12</td>
</tr>
<tr>
<td>0.60 - 0.82(^b)</td>
<td>0.13 ± 0.03</td>
<td>0.37 ± 0.26</td>
<td>0.42 ± 0.29</td>
<td>0.43</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>0.13 ± 0.01</td>
<td>0.17 ± 0.06</td>
<td>0.19 ± 0.10</td>
<td>0.36</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>0.08 ± 0.04</td>
<td>0.17 ± 0.09</td>
<td></td>
<td>0.46</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>0.03 ± 0.01</td>
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<td></td>
<td>0.33</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>0.27 ± 0.02</td>
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<td></td>
<td>0.13</td>
<td>0.14</td>
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<tr>
<td></td>
<td>0.06</td>
<td>0.31</td>
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<td>0.31</td>
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<td></td>
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<td></td>
<td>0.3</td>
<td>0.07</td>
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<td></td>
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<td></td>
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<tr>
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<td>0.29</td>
<td></td>
<td>0.29</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.26</td>
<td></td>
<td>0.26</td>
<td>0.04</td>
</tr>
</tbody>
</table>

\(^a\)Cativa Milk; \(^b\)Polly Milk

where, \(N_{L_{\text{min}}}\) represents the minimum net area, and assumes the value \(N_{L_{\text{min}}} = 4.66\sqrt{F_L}\), with \(F_L\) as the net background in the region of the gamma line of interest.

With the objective of analyzing the density influence on the detection efficiency, five samples with different compaction degrees were prepared.

The obtained densities were: 0.5270 ± 0.0011, 0.5880 ± 0.0012, 0.6480 ± 0.0014, 0.68070 ± 0.0014, 0.6880 ± 0.0015 g/cm\(^3\). From the detection efficiency values calculated by Eqs (2) and (3), the variation of this efficiency with the sample density was analyzed. Fig. 2 shows the data adjustment for the \(^{40}\)K line, obtained from the five samples with
different densities, as listed in the paragraph above. The total deviation of each point was about 25%.

Analyzing the count efficiency variation for the density interval ranging from 0.534 to 0.596 g/cm³, which was the density range of the samples not compacted, a difference of 7% was obtained, a factor to be considered at the samples activity calculation

The system detection efficiency was also calculated employing an $^{152}$Eu certified source, sealed in aluminium. The efficiency $\varepsilon$ was obtained by the relation

$$\varepsilon_i = \frac{N_{ij}}{A_{i} P_{i} \frac{1}{e - \mu_i \frac{A}{A_i}} \cdot \Phi \cdot \tau} \quad \ldots(5)$$

where $\varepsilon_i$ is the intrinsic efficiency for the energy $i$, $N_{ij}$ the net count under the energy peak $i$, $A_i$ the activity under the detector solid angle $\Phi$ in Bq, $P_i$ the absolutely transition probability for gamma
decay through the selected energy for $\varepsilon$, $t$ the count time, $\mu^{ni}_i$ the aluminium attenuation coefficient for the energy $i$, calculated with the XCOM Software, $x^{AI}$ the detector aluminium layer thickness, which is 1.7 mm, $f$ the self-absorption factor of the source aluminium layer, supplied by the source manufacturer, $\tau$ the dead time correction.

Employing Eq.(5), the system efficiency was calculated for each observed energy peak, obtaining the graph presented in Fig. 3. Two more samples were also prepared with contaminated milk by Chernobyl's accident, in order to compare them with the measurements of ordinary milk.

Results

Considering the self absorption factor $f$, the radionuclides activity of the samples was calculated according to the expression

$$A = \frac{\alpha N t f}{mt} \ldots (6)$$

where $A$ is the radionuclide activity of interest, $t$ the count time (172800 s), $m$ the net sample mass, $N_t$ the net count under the analyzed radionuclide peak and $\alpha$ the calibration factor calculated with the calibrated samples.

It was possible to identify clearly in the milk samples spectra the 1460.8 keV line of $^{40}$K, though with some difficulty due to the very low activity, the 661.22 keV ($^{137}$Cs) and 2614.4 keV ($^{208}$Tl) lines. The minimum detectable activity for these three lines was 2.3, 3.5 and 0.4 Bq/kg, respectively.

A spectrum of the Cativa Milk, that is very similar to the Polly Milk, is shown in Fig. 4 and as the $^{137}$Cs activity is near the MDA value and the background is relatively high, the peak is not visible. The obtained results for the Cativa Milk and Polly Milk can be seen, in a summarized form in Table 2. Six samples of each brand of powdered milk trademark were prepared and three repetitions for each sample were performed. In order to verify the statistical equivalence between these 18 measurements, a statistical analysis was done employing the statistical software.

First the data normality was analyzed. Once this is done, it was used as standard for the statistical tests. The normality for both groups of concentration data, from Cativa and Polly milks, was verified for $^{40}$K. Based on this condition, the Tukey's average comparison test was applied on the obtained activity values and demonstrated that no statistical difference exists. The test of Tukey is a method for multiple comparisons used to test any contrast between averages values in experiments where many variations are present randomly. At a 95% confidence level, the activity values of the 18 measurements of each milk brand can be considered the same, taking into account the range of the experimental deviations.

A spectrum of $^{137}$Cs contaminated milks from Ceteco and Dano Milk is shown in Fig. 5. Comparing Fig. 5 with Fig. 4, the difference between contaminated milk and normal milk is evident. In Table 3 these results are compared with some measurements performed with national and imported milks from Brazil, and with measurements performed in Venezuela. All of the measurements employed the same technique of the present work, with little difference in the geometry due to sample volume.

Table 4 shows the comparison of these results for $^{137}$Cs with data of "in natural" milk measurements, realized in the region of a nuclear power station in Rio de Janeiro. Columns 2, 3 and 4 of Table 4 show some results of milk collected from three farms during the years 1981 - 1982 and analyzed by two different institutes. Columns 5 and 6 give the annual mean results of monitoring measurements from 1981 to 1996. All the data of this table was obtained from ash samples measured in a HPGe detector. For this comparison, the results presented at Table 2 were properly converted to liquid milk, employing the reduction factor of 8.5 (8.5 liter of natural milk to produce one kilogram of powdered milk), supplied by the producer.

| Table 5 — $^{40}$K, $^{137}$Cs and $^{232}$Th activities in milk samples |
|--------------------------|--------------------------|--------------------------|
| $^{40}$K (Bq/L) | $^{137}$Cs (Bq/L) | $^{232}$Th (Bq/L) |
| Cativa Milk | 55 ± 2 | 0.82 - 1.32 | 0.29 - 0.44 |
| Polly Milk | 53 ± 2 | 0.60 - 0.82 | 0.19 - 0.42 |
| Hong Kong Milk | 48 ± 1 | 0.01 - 0.08 | < 0.1 |

At Table 5 is presented a comparison with a work done in Hong Kong. The concentrations have been determined using low background gamma-ray spectrometry and an n-type HPGe detector with 25% relative efficiency. From Tables
3-5, it can be concluded that the obtained results for $^{40}$K, $^{137}$Cs and $^{232}$Th in Cativa and Polly milk, are within the range of activities measured for these radionuclides in other milk brands in Brazil and abroad.

Conclusions

The radionuclides $^{40}$K, $^{137}$Cs and $^{232}$Th were identified in the Cativa and Polly milk sample spectra. As the samples were in secular equilibrium, the $^{232}$Th activity was calculated from the $^{208}$Tl data. The statistical data analysis presented the measurement quality and showed the equivalence among the repetitions.

It can be concluded that, in general, the implemented technique presented good results when compared with other literature data. This study showed that the radioactivity levels of Cativa and Polly milk are well below the maximum levels permitted by CNEN$^{13}$ (Brazilian National Commission of Nuclear Energy), that is 370 Bq/kg for $^{137}$Cs, and can be usually consumed without any restriction.

References

6 Set of 8 calibrated gamma-emitting sources (SEM-A2), International Atomic Energy Agency; Eletronics and Measurement Section, Vienna, 1982.
13 CNEM-NE-3.01, Basic appointments of radioprotection, July 1988.