

**INSTRUMENTAL ANALYSIS BY GAMMA
SPECTROMETRY OF LOW LEVEL
CAESIUM-137 IN MARINE SAMPLES**



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R.C.L. FIGUEIRA, L.R.N. SILVA,
A.M.G. FIGUEIREDO, I.I.L. CUNHA
Instituto de Pesquisas Energéticas e Nucleares
IPEN-CNEN/SP,
Radiation Chemistry Supervision,
São Paulo,
Brazil

Abstract

**INSTRUMENTAL ANALYSIS BY GAMMA SPECTROMETRY OF LOW LEVEL CAESIUM-137
IN MARINE SAMPLES.**

An instrumental method for the analysis of low levels of ^{137}Cs in marine samples consists in calibrating the detector, determining the counting efficiency of the detector, accumulative counts of background and sample and smoothing the 661.6 keV photopeak. The methodology was applied to reference samples containing low levels of ^{137}Cs , showing a good accuracy. It was further applied to sediment samples from the southern coast of Brazil. The levels obtained ranged between 1.0 and 1.8 $\text{Bq}\cdot\text{kg}^{-1}$, and the lower limit of detection and minimum detectable concentration values were 10 mBq and 0.28 $\text{Bq}\cdot\text{kg}^{-1}$, respectively.

1. INTRODUCTION

As other sources of pollution, radioactive pollution is of great environmental concern. Humans and living organisms can be affected by anthropogenic radionuclides, which are distributed around the world through radioactive fallout derived from weapons tests, the activities of the nuclear power industry and nuclear accidents.

In this context, it is necessary to perform monitoring programmes in order to obtain the radionuclide levels in the environment. The analysis of radionuclides present in low levels in the environment usually requires tedious and laborious radiochemical methods which consist in dissolving the sample, concentrating the obtained solution, eliminating the interferences and counting.

An alternative method to the gamma emitting radionuclides analysis is to resort to instruments, but this presents a series of difficulties related to background counts [1] (fluctuations in the background are identified as true photopeaks), a low detection limit of the detector and the change in the photopeak position. All of these factors may act as sources of error in the analysis of the gamma spectrum, especially when small photopeaks are formed.

Many authors have studied ways to minimize the interferences due to background radiation and improve the detection limit and the precision of the analysis by using smoothing procedures and detectors with anticoincidence systems [2, 3].

To fulfil these aims, an instrumental method for the analysis of ^{137}Cs in marine samples was developed, as caesium is a critical radionuclide from a radiological point of view.

The method consists in calibrating the detector, determining the detector counting efficiency, accumulative counts at regular time intervals of both sample and background and smoothing the 661.6 keV ^{137}Cs photopeak.

The MAESTRO II computer software [4] offers several programmes for such a purpose, so it was possible to load files to carry out the above functions.

2. METHODOLOGY

2.1. Equipment

The counting measurements were carried out with a high purity Ge detector (ORTEC, Model GEM 60120P) with a resolution of 1.9 keV at a 1332.40 keV photopeak of ^{60}Co . The software used for the gathering of data was MAESTRO II.

2.2. Detector calibration

A detector calibration was performed using several gamma ray emitting nuclides, in particular ^{137}Cs (661.6 keV) and ^{60}Co (1332.4 keV).

2.3. Reference samples

In order to verify the precision and accuracy of the analysis method, the following food and environment samples were taken in accordance with the 1989 International Atomic Energy Agency classification: IAEA-375 (marine sediment), Soil-6 (soil), IAEA-307 (seaweed), IAEA-352 (tuna fish) and IAEA/SD-N-2 (marine sediment).

2.4. Detector counting efficiency

To determine the detector counting efficiency in the ^{137}Cs photopeak region, the IAEA-375 reference value was employed (5281 Bq·kg⁻¹ of ^{137}Cs).

The sample was dried in a muffle at 110°C for 8 hours, transferred to plastic recipients (5 cm in diameter, with variable heights of 2, 2.5 and 3 cm). After weighing, the samples were counted for six hours. The gamma spectrum was analyzed using the VISPECT2 software [5], and the counting efficiency was calculated using the following relation:

$$\varepsilon = \frac{C_R}{t \cdot m_R \cdot A_R} \quad (1)$$

where

- ε is detector efficiency to the 661.6 keV photopeak of ^{137}Cs ,
- C_R is the net counting of ^{137}Cs in the reference sample,
- t is the counting time in seconds,
- m_R is the mass of the reference sample (g),
- A_R is the activity of the reference sample (Bq·g⁻¹).

The results are shown in Table I. There is no significant variation of the detector efficiency, as the height of the sample in the standard plastic recipient varied between 2 and 3 cm. Therefore, in order to improve the counting statistics, it is better to count samples of a height of 3 cm, rather than 2 cm, as this allows for a greater sample quantity to be counted.

TABLE I. DETECTOR EFFICIENCY TO THE 661.6 keV (^{137}Cs) PHOTOPEAK FOR DIFFERENT SAMPLE HEIGHTS

Height (cm)	Mass (g)	Efficiency (%)
2.0	58.29	2.170 ± 0.009
2.5	67.61	2.075 ± 0.012
3.0	80.72	1.923 ± 0.013

2.5. Background radiation

The environmental samples present low activity, so any background radiation has an influence on the detection of the radionuclide. For this project, a study was conducted of the variation of the background radiation in the region of the ^{137}Cs photopeak in function of time.

Using the MAESTRO II software for the acquisition of data, it was possible to obtain background counts at intervals of 10 000 to 200 000 seconds for a total counting time which varied from 70 000 to 250 000 seconds. In order to improve counting statistics, the counting time depended on the level of ^{137}Cs in the sample.

The gamma spectrum was smoothed according to a binomial algorithm which replaces the original data channel by channel with the smoothed data as follows:

$$S_i = \sum_{j=1}^5 C_j \cdot O_{i-3+j} \quad (2)$$

where:

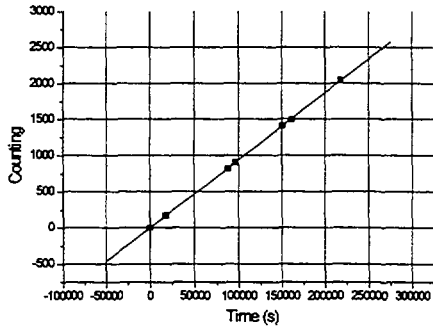
- S_i is smoothed data in the channel i ;
- C_j is the smoothing coefficient;
- O_i is the original data in channel i .

It was noticed that the ideal number of channels for the analysis was eleven. The ^{137}Cs photopeak was set so as to be positioned in the channel between 2641 and 2651. Any variation in the channel versus energy function could lead to an error in the analysis (change in the photopeak of ^{137}Cs). Therefore, the spectrum often had to be recalibrated to the channel position previously specified.

Figure 1 presents the background counts in the ^{137}Cs photopeak region, the counting time, the angular coefficient and respective standard deviation (σ_{BG}).

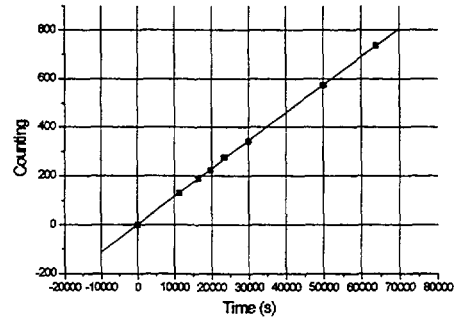
2.6. ^{137}Cs analysis in the reference materials

Reference samples (weighing 75 g to 105 g) were dried in the muffle at 110°C , transferred to plastic recipients (5 cm in diameter, 3.0 cm in height), weighed and counted in the Ge detector. Accumulative countings were recorded in intervals of 10 000 seconds, with the total counting time ranging from 25 000 to 150 000 seconds.



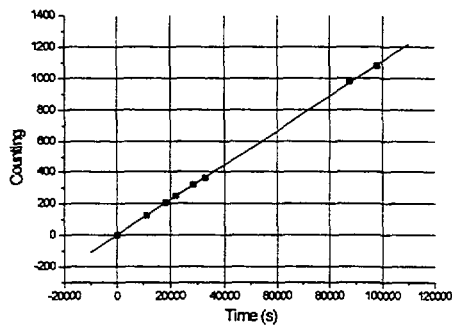
$$Y = (93.4 \cdot 10^{-4} \pm 0.4 \cdot 10^{-4}) X + (1.2 \pm 4.5)$$

FIG. 1. Background counts at the ^{137}Cs photopeak region, of time.



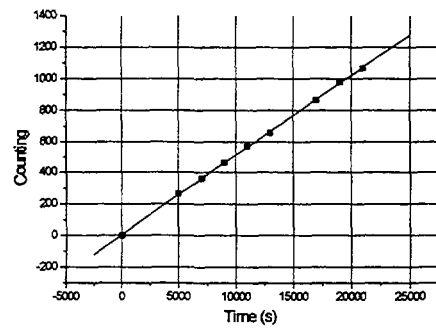
$$Y = (114.9 \cdot 10^{-4} \pm 0.6 \cdot 10^{-4}) X + (1.0 \pm 1.9)$$

FIG. 2. ^{137}Cs counts for seaweed (IAEA-307) as a function of time.



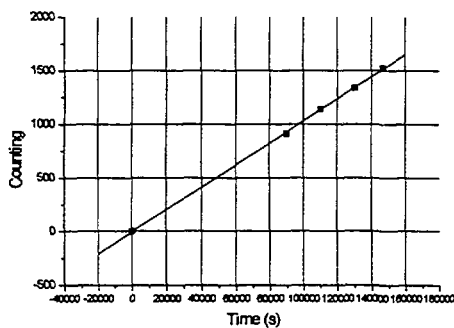
$$Y = (110.6 \cdot 10^{-4} \pm 0.5 \cdot 10^{-4}) X + (1.3 \pm 2.6)$$

FIG. 3. ^{137}Cs counts for tuna fish (IAEA-352) as a function of time.



$$Y = (50.8 \cdot 10^{-3} \pm 0.3 \cdot 10^{-3}) X + (5.4 \pm 4.3)$$

FIG. 4. ^{137}Cs counts for soil (Soil-6) as a function of time.



$$Y = (103.5 \cdot 10^{-4} \pm 0.9 \cdot 10^{-4}) X - (4.8 \pm 10.2)$$

FIG. 5. ^{137}Cs counts for marine sediment (IAEA/SD-N-2) as a function of time.

The ^{137}Cs activity was calculated according to the following equation:

$$(A_{cs} \pm \sigma_{cs}) = \frac{(C_s \pm \sigma_s) - (C_{BG} \pm \sigma_{BG})}{m_A \cdot t \cdot (\varepsilon \pm \sigma_\varepsilon)} \cdot 1000 \quad (3)$$

where

- A_{cs} is the ^{137}Cs activity in the sample ($\text{Bq}\cdot\text{kg}^{-1}$),
- σ_{cs} is the standard deviation of ^{137}Cs activity in the sample,
- C_s is the ^{137}Cs gross counting in the sample,
- σ_s is the standard deviation of ^{137}Cs counting in the sample,
- C_{BG} is the background counting,
- σ_{BG} is the standard deviation of background counting,
- m_A is the mass of sample (g),
- t is the counting time(s),
- ε is the counting efficiency at the ^{137}Cs photopeak (661.6 keV), as determined by equation (1).

Figures 2 to 5 show the ^{137}Cs counts in the reference samples, as a function of time. These figures reveal that in all cases, the angular coefficients were higher than those obtained for background radiation, thus showing that the method developed was adequate for the analysis of ^{137}Cs with the aid of instruments. Table II presents the results of the ^{137}Cs analysis in the reference samples.

The results show that the reference samples containing a ^{137}Cs level of about $3 \text{ Bq}\cdot\text{kg}^{-1}$ present a relative error of 23% which decreases to 0.6% as the ^{137}Cs level reaches $50 \text{ Bq}\cdot\text{kg}^{-1}$. This is better visualized in Figure 6, which illustrates the ratio between the experimental and the certified values.

TABLE II. ANALYSIS OF ^{137}Cs IN REFERENCE MATERIALS ($\text{Bq}\cdot\text{kg}^{-1}$)

Reference material	Certified value	Obtained value	Standard deviation ^a (%)	Error ^b (%)
Soil-6	53.65 (51.43–57.91)	54 ± 1	1.8	0.6
IAEA-307	4.9 (4.5–5.2)	4.7 ± 0.5	10.6	4.1
IAEA-352	2.7 (2.5–2.8)	3.3 ± 0.5	15.1	22.2
IAEA/SD-N-2	0.8 (0.5–1.0)	0.61 ± 0.09	14.7	23.8

^a Relative standard deviation.

^b Relative error.

2.7. Lower limit of detection

The lower limit of detection (LLD) [6] was calculated according to the expression:

$$\text{LLD} = \frac{4.66 \times \sigma_{BG}}{\varepsilon} \quad (4)$$

where

σ_{BG} is the standard deviation of ^{137}Cs counting in the sample due to the background radiation in the region of the ^{137}Cs photopeak,
 ϵ is the detector counting efficiency.

The LLD obtained was 10 mBq, which is in good agreement with the values published by Das and Comans [2] and Das [7] and indicates the high sensitivity of the method.

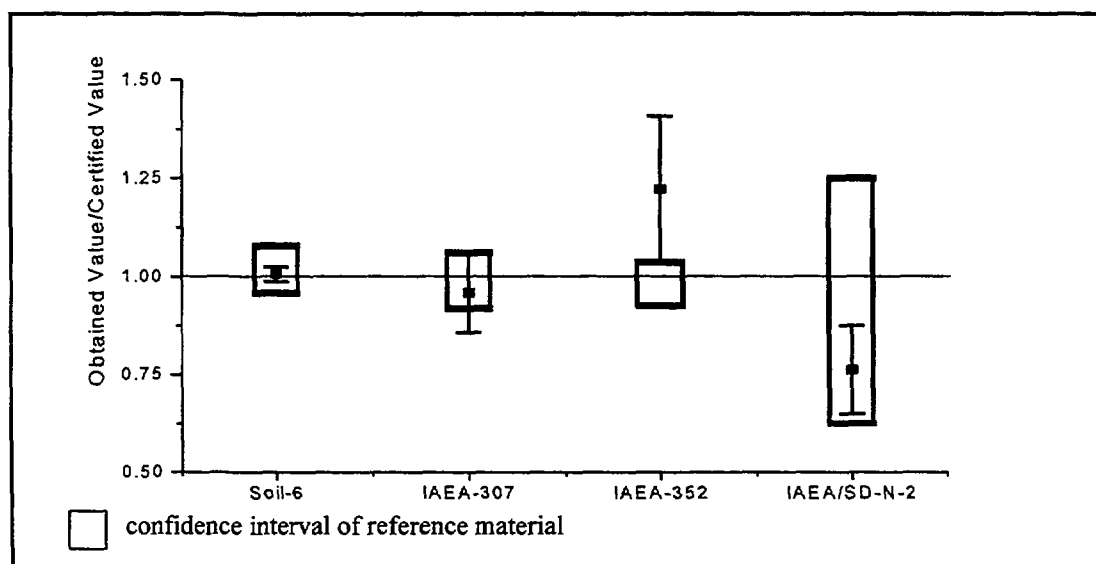


FIG. 6. Ratio of experimental to certified values.

2.8. Minimum detectable concentration

The minimum detectable concentration (MDC) was obtained using the equation:

$$\text{MDC} = \frac{4.66 \times \sigma_A}{\epsilon \times m} \quad (5)$$

where

σ_A is the standard deviation of ^{137}Cs counting in the sample;
 m is the mass of the sample (g).

TABLE III. MDC VALUES IN REFERENCE MATERIALS ($\text{Bq}\cdot\text{kg}^{-1}$)

Reference material	Certified value	MDC
Soil-6	53.65	1.65
IAEA-307	4.9	0.46
IAEA-352	2.7	0.45
IAEA/SD-N-2	0.8	0.28

Table III presents the MDC results obtained in the analysis of reference samples. The values of MDC of Table III were compared with the certified values for ^{137}Cs in the reference materials. It can be concluded that this methodology provides good results for the analysis of this radionuclide even when low levels are present, as for marine sediment ($0.8 \text{ Bq}\cdot\text{kg}^{-1}$). Furthermore, MDC is important to establish threshold limits for the determination of the ^{137}Cs concentration.

2.9. ^{137}Cs analysis in Brazilian marine sediments

Marine sediments were collected along the southern coast of Brazil by the Oceanographic Institute of the University of São Paulo.

These samples were analysed as described in section 2.6 above. The ^{137}Cs levels varied from 1.0 to $1.8 \text{ Bq}\cdot\text{kg}^{-1}$ with a relative pattern of deviation of 2% to 14%. Figure 7 presents the ^{137}Cs levels assessed in marine samples collected at different depths in Brazilian waters. These levels are lower than in other regions of the world which are affected by radioactive effluents from nuclear reactors, reprocessing plants and the Chernobyl accident.

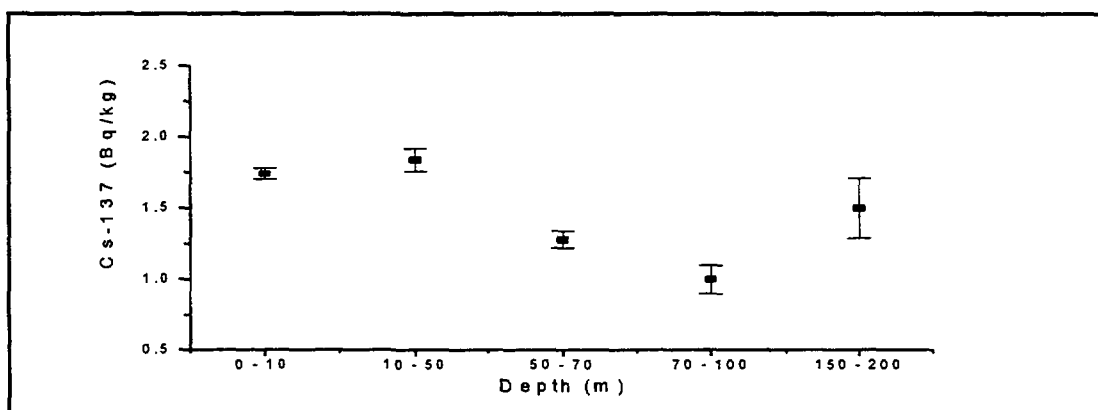


FIG. 7. Variation of ^{137}Cs levels with the sampling depth.

The levels found in Brazilian coastal waters are due to global fallout, i.e. radionuclides released from atomic explosions which were distributed worldwide through the action of atmospheric winds.

The levels of ^{137}Cs in Brazilian marine samples were compared with those of other regions of the world [8–11] and are presented in Figure 8. The data obtained in the present study are used as ^{137}Cs reference levels in Brazilian marine sediments; any alteration in these values can be attributed to a specific cause such as, for instance, an accident or an increase in the fallout level.

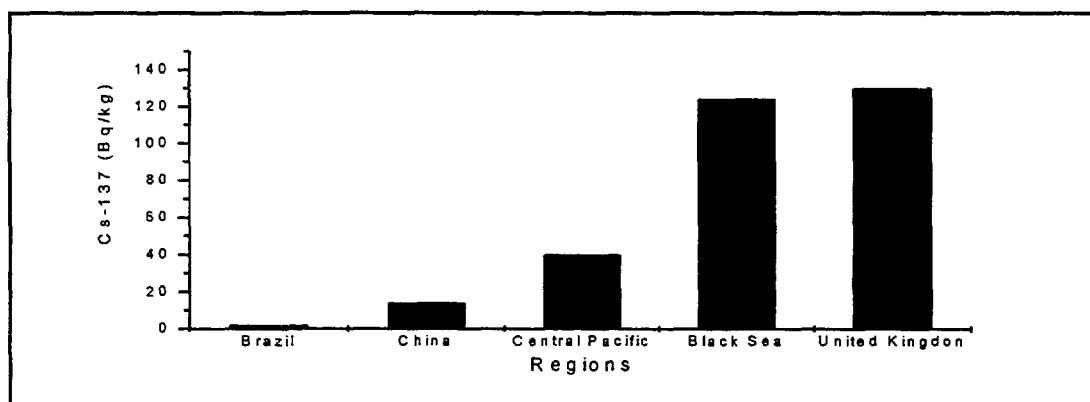


FIG. 8. Levels of ^{137}Cs in Brazilian marine sediments compared with the levels found in other regions of the world.

3. CONCLUSION

The methodology described shows good results in the determination of low levels of ^{137}Cs , and eliminates the need for laborious and tedious radiochemical methods.

Concentrations of ^{137}Cs in Brazilian marine sediments are very low. Their analysis by an instrumental method that does not include the procedures of detector recalibration, smoothing and accumulative countings is impracticable or presents errors as high as 200%. However, using the procedures outlined, it was possible to analyse ^{137}Cs levels as low as $0.8 \text{ Bq}\cdot\text{kg}^{-1}$ with a standard deviation of 14%.

The outcome of the reference samples analysis showed a good degree of precision and accuracy. Similarly, the LLD and MDC values obtained indicate that the methodology is favourable for routine monitoring purposes, especially in instances where small photopeaks appear in the gamma spectrum.

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