This article brings the results of a method for quality assurance in gamma-ray spectrometry of seabed sediments. Sediments were collected in selected locations of the South and Middle Adriatic Sea using grab and corer tools. Using our own experimental design, we determined the self-attenuation factors of selected samples. The article also discusses sources of uncertainty in gamma-ray spectrometry, which is another important issue in quality assurance. Together with self-attenuation correction sources of uncertainty are used to calculate the activity concentration for a given sample. The presented procedure demonstrates how a gamma-ray spectrometry experiment should be approached in order to properly account for errors and uncertainties specific to a particular sample.

KEY WORDS: $^{137}$Cs, measurement uncertainty, self-attenuation

Gamma-ray spectrometry is a common method used by laboratories for environmental radioactivity monitoring to determine activity concentrations of radionuclides in standardised sample geometries (Marinelli beaker, cylindrical geometries, etc.). In principle, one should calibrate the measurement setup for every geometry used, which should be done with a variety of calibration sources in order to reproduce specific photon attenuation effects for each measured sample (1). In most laboratories, samples are prepared in the same shapes and sizes but there is a considerable variation in sample density and composition. This variation is resolved by sample-specific corrections known as self-attenuation factor (2). In this study we used $^{137}$Cs as an example for calculating activity concentration and related uncertainty. $^{137}$Cs is one of the most frequently measured radionuclide in environmental samples. In seabed sediments it is widely used to calculate sedimentation rate. The aims of this study were to address the issue of sampling seabed sediments, to simplify the method for direct determination of the self-attenuation factor (which is the most important correction factor for this kind of samples), and to determine sources of uncertainty in gamma-ray spectrometry of the seabed sediments.

MATERIALS AND METHODS

Sediment sampling and preparation of samples for measurements

Sediments used in this study were collected during the “International Scientific Cruise to Adriatic and Ionian Seas” organised by International Atomic Energy Agency (IAEA) under a Technical Cooperation Project RER/7/003, which took place on 17-28 September 2007. Samples were taken from seven locations in the Middle and South Adriatic using a grab sampler and a box corer. Shipek grab sampler ($\approx$ 50 kg) collects a 3 L sample from a sampling area of around 400 cm$^2$. For corer sampling, a non-destructive analytical technique on an undisturbed sediment column was used, and the column was sliced into...
cylindrical segments. The slicing intervals are chosen with respect to the average settling rate over a time scale of interest. In this work, the column was sliced every 2 cm, so that each slice contained 100 mL of dry sediment, which was compatible with the geometry of calibration source in our laboratory.

When the central core of a sediment sample is sliced, the slices are considered to be different samples. After homogenisation by grinding in a mill, the slices were dried at 60 °C to 80 °C for 3 to 10 days to obtain constant weight (3).

When sampling sediment slices, it is necessary to determine the thickness of the slice. It is also important to measure the humidity of the sample and take into account weight loss after drying the sample. The slice that is dried to a constant weight should be the size of the geometry used for gamma-ray spectrometry. If the slice is smaller, the geometry will not be fulfilled and if the slice is larger, the exceeding portion of the sample will not be analysed.

Gamma-ray spectrometry

For gamma-ray spectrometry we used an ORTEC High-purity Germanium Coaxial Photon Detector System (USA; resolution of 2.24 keV at 1330 keV \(^{60}\)Co, relative efficiency of 74.2 % at 1330 keV) connected to a multichannel analyser. This system is routinely used for soil, pebble, and rock sample analysis. The detector is protected with a shield made of 10-cm thick lead layer overlaid by a 2-mm thick copper foil and a 2-mm thick cadmium foil. Energy and efficiency calibrations were performed using calibration sources (Czech Metrology Institute) covering energies from 80 keV to 2500 keV. Due to a limited volume of the samples, 100 mL plastic cylindrical containers were used.

The counting time for samples was 80,000 s. Regular checks were made for stability of the spectrometer, and the energy calibration was always rechecked against a standard source (ER X standards: mix of \(^{241}\)Am, \(^{109}\)Cd, \(^{137}\)Ce, \(^{57}\)Co, \(^{60}\)Co, \(^{137}\)Cs, \(^{113}\)Sn, \(^{88}\)Sr, \(^{88}\)Y, \(^{203}\)Hg). Measurement results include careful evaluation of the full analytical procedure and the analysis of uncertainty.

Calculating the activity concentration

Equations 1 to 7 given by Dovlete and Povinec (4) are standards for calculating the activity concentration \(A\) (or specific activity) of a gamma-emitting radionuclide in environmental samples.

The activity concentration \(A\) (or the specific activity) of a gamma-emitting radionuclide in a sample is calculated as:

\[
A = \frac{N}{\epsilon \cdot \gamma \cdot t_s \cdot m \cdot K_1 \cdot K_2 \cdot K_3 \cdot K_4 \cdot K_5},
\]

where:

\(N\) is the corrected net peak area of the corresponding photopeak, obtained with the following equation:

\[
N = N_s - \frac{t_s}{t_b} N_b,
\]

where:

\(N_s\) is the net peak area in the sample spectrum; \(N_b\) is the corresponding net peak area in the background spectrum; \(\epsilon\) is the efficiency at photopeak energy; \(t_s\) is the live time of the sample spectrum collection in seconds; \(t_b\) is the live time of the background spectrum collection in seconds; \(m\) is the mass of the measured sample in kilograms; and \(\gamma\) is the emission probability of the gamma line corresponding to the peak energy.

\(K_1\) is a correction factor for the nuclide decay over a time \(\Delta t\) elapsed from the sample collection to the start of the measurement, and is obtained with the following equation:

\[
K_1 = \exp\left(-\frac{\ln 2 \cdot \Delta t}{T_{1/2}}\right),
\]

where \(T_{1/2}\) is the radionuclide half-life.

\(K_2\) is a correction factor for the nuclide decay during the counting period, and is obtained with the following equation:

\[
K_2 = \frac{T_{1/2}}{\ln 2 \cdot t} \left(1 - \exp\left(-\frac{\ln 2 \cdot t}{T_{1/2}}\right)\right),
\]

where \(t\) is the duration of the measurement.

\(K_3\) is the self-attenuation factor, representing a correction for self-attenuation in the measured sample relative to a reference calibration sample. It is defined as

\[
K_3 = \frac{\epsilon(\mu, E)}{\epsilon(\mu_{ref}, E)},
\]

where \(\epsilon(\mu, E)\) is the full energy \((E)\) peak efficiency for a sample with a linear attenuation factor \(\mu\), and \(\epsilon(\mu_{ref}, E)\) is related to a reference sample with \(\mu_{ref}\). Evidently, if the matrix of both the calibration sample and the measured sample is the same, then \(K_3 = 1\).

\(K_4\) is a correction factor for the loss of pulses due to random summing, and is obtained with the following equation:
\[ K_s = \exp(-2R\tau), \]  

where \( \tau \) is the resolution time of a measurement system and \( R \) is the mean count rate. For low count rates, this correction factor can be 1.

\( K_s \) is a coincidence correction factor for nuclides which decay through a cascade of successive photon emissions. It is defined as a ratio of the corresponding apparent efficiency \( \epsilon_{ap}(E) \) and the full energy peak efficiency \( \epsilon(E) \):

\[ K_s = \frac{\epsilon_{ap}(E)}{\epsilon(E)}. \]  

If a nuclide does not produce a cascade of gamma-rays, then \( K_s = 1 \). Generally, \( K_s \) depends on nuclide decay scheme, sample geometry and composition, and detector parameters.

A gamma photon which propagates through a material, including the sample in which it has been generated, undergoes interactions that occur with a given probability. In these interactions, the photon is either absorbed or scattered, thus losing energy. Hence, there are photons which do not contribute to the peak count rate. The level of self-attenuation depends on a number of parameters, for example on sample geometry and on \( \mu \) which, in turn, depends on material density, sample composition, and photon energy (2). The corrected peak areas are the spectrum peak areas multiplied by the correction as (5):

\[ A = A_0 e^{-\mu x}, \]  

where:

- \( A \) is the activity concentration at energy \( E \); 
- \( \mu \) is the table value at energy \( E \); normally the mass attenuation factor; and 
- \( x \) is the length of the path of a gamma ray.

In environmental analyses, \( \mu \) is usually not known \textit{a priori} and is therefore estimated experimentally (1) or calculated according to assumed sample composition and density (6). Distribution of the path lengths for the photons contributing to the peak count rate depends mainly on sample geometry and less on detector dimensions and photon energy.

**Standard methods for determination of the self-attenuation factor**

The verified method by Sima and Dovlete (1) uses point source for calculating self-attenuation. First we calculated self-attenuation between the source and the vacuum (the attenuation factor for the source is known), and then between the vacuum and the sample. To calculate the self-attenuation factor (\( K_s \)), Sima and Dovlete (1) use the following equation:

\[ K_s = \frac{1}{\int_{V} dV \int_{\Omega} d\Omega N(\vec{r}) e^{-\mu x} T_s(E, \vec{r}, \Omega) p_t(E, \vec{r}, \Omega)} \int_{V} dV \int_{\Omega} d\Omega N(\vec{r}) T_o(E, \vec{r}, \Omega) p_t(E, \vec{r}, \Omega). \]  

where \( N(\vec{r}) dV \) is the emission rate for photons of energy \( E \) from the volume element \( dV \); \( \vec{r} \) and \( \Omega \) are the initial coordinate and direction of photon propagation; \( x(\vec{r}, \Omega) \) is the photon path length through the source; \( T_s(E, \vec{r}, \Omega) \) is the probability of the absence of interaction in the media interposed between the source and the sensitive volume of the detector; and \( p_t(E, \vec{r}, \Omega) \) is the probability of photon detection in the sensitive volume of the detector.

Another similar method based on transmission measurements that can be easily done in any laboratory was proposed by Cutshall et al. (6). In this method, a standard point source is positioned above a sample which is located on the detector, and the number of counts in the full energy peak is measured. In this case, the self-attenuation factor can be calculated from

\[ F_s = \frac{\ln(A/A_0)}{1 - (A/A_0)}, \]  

where \( A \) and \( A_0 \) are the peak count rates for the actual sample and a reference sample, respectively.

Two basic approaches have been applied for solving the problem of self-attenuation in the volume of a sample: experimental (6, 7) and mathematical - using Monte Carlo simulations (1, 8).

One of the aims of this work was to simplify the method for direct determination of self-attenuation in environmental samples.

**Simplified method for determination of the self-attenuation factor**

Earlier, most calibrations were carried out using a point source positioned in the air above the detector, so the attenuation factors were calculated relative to air. In our case, calibration was performed using an aqueous solution of \( ^{137}\text{Cs} \) in a container of the same geometry as for distilled water and sediment samples.

This simplifies and speeds up the method because no calculation of attenuation factors sample/air and standard/air is needed. In measurements, a point source of \( ^{137}\text{Cs} \) was first placed directly on top of a container with distilled water and counted for 1000 s (2). This way we determined \( A_0 \). Sediment samples...
were prepared as described before and placed into containers of the same geometry as for distilled water. The samples were counted for 1,000 s with the point source on top, and 80,000 s without the point source. Namely, the activity of the point source is much higher in relation to the activity of the sample, so counting 1,000 seconds is sufficient. Without the point source, our laboratory practice has shown that 80,000 seconds is optimal counting time for the samples. Attenuation factor was calculated using the following equation:

\[ F_a = \frac{A_0}{A} \]  

**Measurement uncertainty**

Identification of sources of uncertainty is an important step in obtaining high quality data, and in gamma-ray spectrometry the standard procedure used for calculating measurement uncertainty is described by Dovlete and Povinec (4). The sources of uncertainty can be grouped into four categories according to their origin: uncertainties related to test preparation, to energy and efficiency calibration, to test measurements, and to nuclear data. Uncertainty is reported as standard uncertainty, combined standard uncertainty, or expanded uncertainty (4, 9).

Activity concentration of radionuclides is a function of several quantities (detector efficiency, gamma ray emission probability, counting rate, correction factors, etc.), and each of these quantities has an associated uncertainty (10). The combined standard uncertainty \( u_c \) of a quantity \( y \) of interest can be derived by applying the Gauss' law of the propagation of uncertainty

\[ u_c(y(x_1, \ldots, x_n)) = \sqrt{\sum_{i=1}^{n} \left( \frac{\partial y}{\partial x_i} \right)^2 (u(x_i))^2} , \]  

where \( y(x_1, x_2, \ldots, x_n) \) is a function of several quantities \( x_1, x_2, \ldots, x_n \). This equation is valid if the quantities \( x_i \) are independent and if \( u(x) \ll x \).

Energy calibration establishes a relation between the peak position in the spectrum and the corresponding gamma-ray energy. This simple and yet critical step is normally performed before a sample is measured. In practice, energy calibration curve is used mainly to identify radionuclides, and the uncertainty in energy is in most cases disregarded as an error source.

Uncertainties coming from efficiency calibration, on the other hand, cannot be neglected. Most algorithms used for efficiency calibration assume that the true efficiency function can be represented by a fitted analytical function. However, a correct allocation of uncertainties to an interpolated efficiency value is a complex problem. The uncertainty of an efficiency value calculated using an interpolation function cannot be obtained from uncertainties in the fit parameters alone. Possible correlations between measured input efficiency data should be considered as well (11). There can also be energy regions where the true efficiency curve systematically deviates from the fitted curve. This systematic difference is seldom included in the uncertainty computed by algorithms.

Regarding gamma-ray emission probabilities, data for a limited number of radionuclides can be found in IAEA-TECDOC-619 (12) and in Firestone and Shirley (13). In some cases, the related uncertainty can be a major contributor to the combined uncertainty.

Literature data on uncertainty in half-life should be used to calculate its contribution to the combined uncertainty of a measurement result. In principle, published data on half-life are less reliable than those on gamma-ray energies, but the uncertainty in half-life still contributes much less than other uncertainty sources. IAEA TECDOC-619 (12) together with Firestone and Shirley (13) are good sources of data for a limited number of nuclides of interest.

In our laboratory, we minimise error introduced by a measurement procedure by making sure that there is no difference in the counting geometry between a sample and standards.

Even with a good pile-up rejection, there could be some residual random coincidences. Any full-energy photon the pulse of which is summed with another pulse will not be recorded in a single photon peak, which causes a loss of counts. This loss is count rate-dependent, but for low count rates the associated uncertainty can be neglected. If a nuclide (e.g., \( ^{60}\text{Co} \), \( ^{152}\text{Eu} \), \( ^{154}\text{Eu} \), \( ^{133}\text{Ba} \), \( ^{88}\text{Y} \), etc.) emits photons in a cascade, the coincidence effects can be important, especially in case of high-efficiency semiconductor detectors. This is not a trivial problem, but fortunately it does not involve \( ^{137}\text{Cs} \).

In many cases one can neglect uncertainties related to dead-time effects, because counting rates in environmental samples are usually rather low. The same applies to uncertainties associated with decay time effects (measurement time, decay time and counting time), since measurement of time poses no problem.

If the composition and/or density of a sample to be measured differ from those of the calibration...
sample, self-attenuation corrections to efficiency should be applied. As explained earlier, these corrections depend on sample geometry, composition and density, as well as on detector parameters. They are generally stronger for low photon energies, and increase with increasing sample volume, density, and atomic number. This introduces an additional uncertainty, which should be assessed from particular experimental conditions. If most elements in the sample matrix are known, then the relative uncertainty of the self-attenuation correction factor is less than 1% for energies higher than 60 keV and less than 5% for energies lower than 40 keV.

Generally, uncertainty due to counting statistics is one of the most important contributors to total uncertainty. Mathematical procedures for deriving net peak areas are in many cases based on a simple background subtraction, which gives the corrected net peak area:

$$N = N_A - \frac{t_s}{t_b} N_B,$$

where $$N_A$$ is the net peak area in the sample spectrum; $$N_B$$ is the corresponding net area of the background peak (obtained from a separate analysis performed on the background spectrum); $$t_s$$ is the live time of the sample spectrum; and $$t_b$$ is the live time of the background spectrum. In case of overlapping peaks, a matrix solution (14) is most often used to derive the net peak area and related counting uncertainty.

Finally, uncertainty due to sample weighing is estimated either on the basis of information about the balance performance or from a statistical analysis of repeated measurements (4, 9).

RESULTS AND DISCUSSION

Table 1 shows the attenuation factors ($$F_a$$) for one corer and one grab sample. We calculated average activity and uncertainty (coverage factor = 2) from ten repeated measurements. Attenuation factor ($$F_a$$) was calculated using the simplified method (Equation 11). Uncertainty for $$F_a$$ (coverage factor = 2) was determined using Equation 12.

The attenuation factor is in correlation with the atomic number and therefore with the density of the material. The composition of the seabed sediments is

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density / g cm(^{-3})</th>
<th>$$A \pm 2s \times 10^5$$ ((^{137})Cs) / Bq kg(^{-1})</th>
<th>$$F_a \pm 2s$$</th>
</tr>
</thead>
<tbody>
<tr>
<td>dH(_2)O</td>
<td>1.00</td>
<td>(1.30±0.04)E+5</td>
<td>-</td>
</tr>
<tr>
<td>corer</td>
<td>0.91</td>
<td>(1.61±0.04)E+5</td>
<td>0.81±0.07</td>
</tr>
<tr>
<td>grab</td>
<td>0.99</td>
<td>(1.41±0.04)E+5</td>
<td>0.93±0.02</td>
</tr>
</tbody>
</table>

Table 2 Example how to calculate activity concentration and uncertainty

<table>
<thead>
<tr>
<th>Variable name</th>
<th>Value</th>
<th>Uncertainty value / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of the sample / kg</td>
<td>0.101</td>
<td>0.99</td>
</tr>
<tr>
<td>Sampling date</td>
<td>29.09.2007</td>
<td>-</td>
</tr>
<tr>
<td>Measurement date</td>
<td>18.02.2009</td>
<td>-</td>
</tr>
<tr>
<td>$$\Delta t$$ / days</td>
<td>508</td>
<td>-</td>
</tr>
<tr>
<td>Counting time / s</td>
<td>80,000</td>
<td>-</td>
</tr>
<tr>
<td>Half-life / days</td>
<td>10,955</td>
<td>-</td>
</tr>
<tr>
<td>Energy / keV</td>
<td>661.6</td>
<td>-</td>
</tr>
<tr>
<td>Emission probability</td>
<td>0.8462</td>
<td>0.24</td>
</tr>
<tr>
<td>Detector efficiency</td>
<td>0.03064</td>
<td>0.35</td>
</tr>
<tr>
<td>Net peak area</td>
<td>284</td>
<td>0.13</td>
</tr>
<tr>
<td>Correction factor for the nuclide decay from the time the sample was collected to the start of the measurement - $$K1$$</td>
<td>0.96837</td>
<td>-</td>
</tr>
<tr>
<td>Correction factor for the nuclide decay during the counting period - $$K2$$</td>
<td>0.99995</td>
<td>-</td>
</tr>
<tr>
<td>Correction factor for the self-attenuation - $$K3$$</td>
<td>0.81</td>
<td>8.64</td>
</tr>
<tr>
<td>Correction factor for the loss of pulses due to random summing - $$K4$$</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Coincidence correction factor - $$K5$$</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Activity concentration – A / Bq kg(^{-1})</td>
<td>1.74</td>
<td>7.01</td>
</tr>
</tbody>
</table>
usually unknown, so the practice is to correlate the attenuation factor with density (higher density - higher attenuation factor). The analysis of the corer slice mineral composition could simplify and speed up the calculation of attenuation factors within one corer. If the mineral composition and density are similar within one corer, attenuation factor for one slice can be calculated and we could assume it is similar for all the slices (15).

When the obtained $F_a$ are used for $K_1$ in Equation 1, the resulting correction to the activity concentration is less than 10 %, which is in line with literature data (16).

Table 2 shows an example how to calculate activity concentration and related uncertainties for $^{137}$Cs in corer a slice sample. The sample was prepared as described above. Sample mass was 0.1014 kg and volume 100 mL. The geometry used was identical to the geometry of the calibration standard. The activity concentration was calculated using Equation 1, while the uncertainty was calculated using Equation 12.

Although the final values of activity concentrations and their related uncertainties are rounded to two decimal places, for the calculation of these values precise numbers were used. The uncertainties for some values were not taken into account since they do not contribute to the total uncertainty because they are small or not measurable (4).

CONCLUSION

Quality assurance is important for gamma-ray spectrometry. This paper gives an insight into seabed sediment sampling and related problems. To speed up measurement and calculation we have introduced a simplified method for direct determination of the self-attenuation factor. This method can be applied to other environmental samples, along with the estimation of the sources of uncertainties in gamma-ray spectrometry of the seabed sediments, it can be applied to other environmental samples.

Acknowledgement

This study is a part of the research projects “Radioecology of the Adriatic Sea and Coastal Areas” and “Environmental Radioactivity and Radiation Protection” supported by the Croatian Ministry of Science, Education and Sports of the Republic of Croatia and International Atomic Energy Agency (IAEA) TC project RER/7/003 “Marine Environmental Assessment of the Mediterranean Region”.

REFERENCES

Sažetak

OSIGURANJE KVALITETE U GAMA-SPEKTROMETRIJI MORSKIH SEDIMENATA

U ovom radu predstavljena je metoda za osiguranje kvalitete u gama-spektrometriji sedimenata s morskog dna, skupljenih s pomoću grabila i gravitacijske udarne sonde iz odabranih područja srednjeg i južnog dijela Jadranjskog mora. Uzorci za gama-spektrometriju pripremljeni su prema standardnim metodama. Eksperimentalnom metodom razvijenom u našem laboratoriju odredili smo samoatenuacijske koeficijente odabranih uzoraka. Također raspravljamo o izvorima nesigurnosti u gama-spektrometriji kao važnom čimbeniku u osiguranju kvalitete. Zajedno sa samoatenuacijskim koeficijenima, ostali izvori nesigurnosti nužni su za dobivanje potpunog izračuna koncentracije aktivnosti za određeni uzorak. Ovdje predstavljena metoda prikazuje način pristupanja gama-spektrometrijskom mjerenju, kako bismo pravilno objasnili nesigurnosti i korekcije koje potječu iz jedinstvenosti svakog uzorka.

KLJUČNE RIJEĆI: $^{137}$Cs, mjerna nesigurnost, samoatenuacija

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