Verification of $^{90}$Sr determination in marine animals

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Abstract. $^{90}$Sr is considered as a hazardous radionuclide for humans. When it is consumed, it would be eventually accumulated in bone and its daughter, $^{90}$Y, could then harm bone marrow. To monitor $^{90}$Sr in the environment especially in marine food samples it is very important for Thailand as the consumption of marine animals is high and these animals are also exported all over the world and play an important part of the economy. To measure $^{90}$Sr in our food samples, a liquid extraction technique using bis-2-ethylhexyl-phosphoric acid to separate and purify yttrium followed by Cherenkov counting to determine $^{90}$Y in secular equilibrium to $^{90}$Sr were developed at the Office of Atoms for Peace’s laboratory. The analytical performance was validated for all criteria i.e. accuracy, precision and trueness. $^{90}$Sr determination in spiked mussel samples with various activity concentrations in a range of 2 – 1000 Bq kg$^{-1}$ dry weight were performed for statistical evaluation. The results had a relative bias within the accepted relative bias of ± 25% i.e. in the range from 10.36 to 16.98 and passed all criteria. This could confirm our analytical approach for $^{90}$Sr determination in marine animals and foodstuffs was accepted. Moreover the method is cost-efficient, simple and fast to analyse $^{90}$Sr in the samples.

1. Introduction

The $^{90}$Sr presented in the environment is mainly from the atmospheric nuclear weapon tests shortly after World War II in the 1950s and 1960s [1]. Also it has been intentionally and accidentally released into oceans from nuclear reprocessing plants and power plants. This radioactive contamination has been transported and circulated through oceans. $^{90}$Sr has a long physical half-life of 28.79 years ($E_{\text{max}} = 0.546$ MeV) [2] and an effective biological half-life of 18 years [3]. It is considered as a very hazardous radionuclide. It can accumulate in the bones of organisms. It has a highly energetic decay product $^{90}$Y ($E_{\text{max}} = 2.280$ MeV, $T_{1/2} = 64$ h) [2] which can cause damage to bone marrow and may cause Leukaemia and skeletal cancer [4]. This makes $^{90}$Sr contaminated in the environment a highly significant health concern [5]. $^{90}$Sr is therefore one of the most important isotopes to be monitored in our environment, especially the marine environment in Thailand. Since marine animals are consumed in large quantities in Thailand and also these various seafood products are exported to all over the world.

To measure $^{90}$Sr in marine environmental samples a radioanalytical method has to be applied to extract and purify $^{90}$Sr and/or $^{90}$Y from samples and the purified sources which are prepared to be compatible with a specific beta radiation measurement methods. Usually $^{90}$Y in secular equilibrium with $^{90}$Sr is measured to determine $^{90}$Sr which has two source preparations firstly a solid precipitation can be used for measuring gross beta counting with a gas proportional counter and a liquid solution for measuring Cherenkov counting using a liquid scintillation counter (LSC). Cherenkov counting has been wildly applied to measure $^{90}$Y in order to determine $^{90}$Sr [6]. Cherenkov light can only be produced by high energetic beta emitters ($E_{\text{max}} \pm 800$ KeV) i.e. $^{32}$P, $^{36}$Cl, $^{90}$Y and $^{89}$Sr. That means measuring
Cerenkov light could have no interference from possible contaminated low energy beta particles in samples. These could avoid over counting contaminated beta particles in samples which is a common problem of gross beta counting with gas proportional counters. In addition, the Cherenkov samples are acidic solutions which are cheap and simple to prepare and easy to process for waste treatment.

To determine $^{90}\text{Sr}$ via $^{90}\text{Y}$ daughter in marine samples at our institute, the Office of Atoms for Peace (OAP), the liquid-liquid extraction using bis-2-ethylhexyl-phosphoric acid (HDEHP) to prepare $^{90}\text{Y}$ liquid sources and Cherenkov counting using LSC to measure the sources has been developed. This method has already been verified for seawater [7]. The analytical method for animal samples therefore needed to be validated for the accurate and precise criteria which various $^{90}\text{Sr}$ concentrations in spiked mussel meat samples were used to determine the performance for statistical evaluation.

2. Experiment

2.1. Sample description

The mussel samples were collected from Gulf of Thailand, Chonburi province. They were removed from their shells and the mussel meat was dried using a freeze drier method. The three samples, 20 g (dry weight), were spiked with the known activity solution of $^{90}\text{Sr}$ to obtain four activity concentrations i.e. 2 Bq kg$^{-1}$, 50 Bq kg$^{-1}$, 100 Bq kg$^{-1}$ and 1000 Bq kg$^{-1}$.

2.2. Reagent and radioactivity standards

HCl, HNO$_3$, HDEHP, NH$_4$OH, Y(NO$_3$)$_3$, NaOH, toluene, sodium acetate, xylenolorange, KNO$_3$, phenolphthalein and Titriplex III used were analytical grade. $^{90}\text{Sr}$ reference solution (equilibrium $^{90}\text{Sr}^{90}\text{Y}$) was obtained from Eckert and Ziegler Isotope Product.

2.3. Method for determining $^{90}\text{Sr}$ in secular equilibrium to $^{90}\text{Y}$

The radioanalytical method for determining $^{90}\text{Sr}$ in marine animal samples was developed and improved based on Suomela et al. [8]. Aliquot samples were ashed at 610 °C for 15 h. The ash was dissolved with 50 mL of 1 M HCl and added to Y carrier (10 mg yttrium) and the known activities of $^{90}\text{Sr}$ and then boiled for 30 min on hot plate. The samples were filtrated to remove residual. The filtrate was added with citric acid and adjusted to pH 1.5 by adding 6 M NH$_4$OH. For the yttrium separation step, the yttrium in the solution samples was extracted with 50 mL of 10% HDEHP in toluene. The organic phases were washed with the very low concentration HCl i.e. 0.08 M HCl. The yttrium was back extracted using 50 mL of 3 M HNO$_3$. The yttrium in solutions were precipitated in form of Y(OH)$_3$ by adding NH$_4$OH until a pH 9-10 was achieved. The precipitates were removed from solutions by centrifuging and then dissolved with 1 mL of cone.HNO$_3$. The purified yttrium solution samples were transferred into 20 mL plastic vials and made up volume to 15 mL with deionised water for Cherenkov counting. After Cherenkov counting, chemical recovery yields were determined by metal titration using the Titriplex III. The solutions were transferred into Erlenmeyer flasks and made up volume to 20 mL with deionised water. Sodium acetate (1.5 g) and 100 mg of xylenolorange in KNO$_3$ as indicator were added to the samples. Before titrating the samples were adjusted pH 5-6 using 6 M NaOH then titrated until solution colour was changed from red to orange.

2.4. Preparation of calibration source

The $^{90}\text{Sr}$ reference solution (equilibrium $^{90}\text{Sr}^{90}\text{Y}$) which had activity of 1.649 ± 0.051 Bq in 15 mL of HNO$_3$ solution, was contained in a 20 mL polyethylene vial for Cherenkov counting.
2.5. Measurement of $^{90}$Y, counting instrument and software

Cherenkov counting was performed using a PerkinElmer, Tri-Carb 3180 TR/SL. QuantaSmart software was used. The prepared calibration source was counted for 30 min. The energy range from 0 to 50 keV was used to determine counting efficiency from $^{90}$Y. Please note that $^{90}$Y has significantly higher Cherenkov counting efficiency than those of $^{90}$Sr, i.e. 60% and 1% for $^{90}$Y and $^{90}$Sr respectively [9]. Cherenkov counting from $^{90}$Sr therefore could be negligible which means the calibration source, equilibrium $^{90}$Sr/$^{90}$Y solution, could be directly used for determining Cherenkov counting efficiency from $^{90}$Y. The samples were counted with the same protocol and condition as those of the calibration source.

2.6. Data evaluation

Results were analysed using different statistical evaluation i.e. accuracy, precision and trueness based on IAEA criteria [10] as follow:

2.6.1. Accuracy. Accuracy was based on relative bias (RB). The relative bias was between the measured value and the target value calculated as a percentage according to equation (1).

$$B = \left(\frac{\text{Value}_{\text{Measured}} - \text{Value}_{\text{Target}}}{\text{Value}_{\text{Target}}}\right) \times 100$$ (1)

$\text{Value}_{\text{Target}}$ and its associated uncertainty, $\text{unc}_{\text{Target}}$, were the known values.

If the relative bias $\leq$ the Maximum Accepted Relative Bias (MARB) value, the result is considered “Accepted” for accuracy. In this case, the MARB was 25% based on the complexity of radioanalytical method.

2.6.2. Precision and trueness. The precision (P) was calculated according to the following equation.

$$P = \left(\left(\frac{\text{unc}_{\text{Target}}}{\text{Value}_{\text{Target}}}\right)^2 + \left(\frac{\text{unc}_{\text{Measured}}}{\text{Value}_{\text{Measured}}}\right)^2\right)^{1/2} \times 100$$ (2)

The precision would be compared to the Limit of Accepted Precision (LAP) which was 25%. Result was obtained status as “Pass” for precision when:

Figure 1. The Analysis of $^{90}$Sr determination; (A) Mussel meat samples, (B) Ash leaching step, (C) $^{90}$Y extraction by 10% HDEHP (D) Samples in LSC vials for Cherenkov counting.
\( P \leq LAP \) (3)

Result would be scored as “Pass” for trueness when:

\( |\text{Bias}_{\text{relative}}| \leq \frac{\text{Value}_{\text{measured}}}{\text{Value}_{\text{taget}}} \times 2.58 \) \( P \) (4)

2.6.3. The final score result from the test. The final score can be concluded according to the detailed evaluation shown in Table 1.

Table 1. Performance evaluation criteria.

| Accuracy | Precision | Trueness | Final score |
|----------|-----------|----------|-------------|
| Pass     | Pass      | Pass     | Accepted    |
| Pass     | Fail      | Pass     | Warning     |
| Pass     | Pass      | Fail     | Warning     |
| Fail     | Pass/Fail | Pass/Fail| Not accepted|

3. Results and discussion

The analysis results of the spiked samples are shown in Table 2. Individual analysis for each sample looked close together. It should be noted that chemical recovery of the repeated samples had similar values. Also when compared between the samples i.e. 2 Bq kg\(^{-1}\), 50 Bq kg\(^{-1}\), 100 Bq kg\(^{-1}\) and 1000 Bq kg\(^{-1}\), the mean recovery values were quite similar i.e. 69.28, 62.61, 69.28 and 69.28 for 2, 50, 100 and 1000 Bq kg\(^{-1}\) respectively. This can confirm that the method performance was fairly stable. Please note that the detection limits were 1.998 Bq kg\(^{-1}\).

Table 2. The results of \(^{90}\)Sr analysis in spiked mussel samples.

| Sample | Activity (Bq kg\(^{-1}\)) | % Y | Activity (Bq kg\(^{-1}\)) | % Y | Activity (Bq kg\(^{-1}\)) | % Y | Activity (Bq kg\(^{-1}\)) | % Y |
|--------|--------------------------|-----|--------------------------|-----|--------------------------|-----|--------------------------|-----|
| S 2    | 2.055±0.210              | 66.96| 2.451±0.250              | 66.96| 2.250±0.230              | 68.70| 2.252±0.230              | 69.28|
| S 50   | 59.76±3.240              | 62.61| 59.541±3.244             | 61.74| 58.327±3.177             | 63.48| 59.210±3.220             | 62.61|
| S 100  | 116.610±5.680            | 63.48| 116.009±5.681            | 61.74| 119.144±5.797            | 63.48| 117.254±5.720            | 62.90|
| S 1000 | 1143.389±48.156         | 71.30| 1155.517±48.767          | 67.83| 1191.470±50.212          | 68.70| 1163.459±49.044          | 69.28|

The performance evaluation of the spiked samples is shown in Table 3. All results had relative bias in a range of 10.36 – 16.98 which was below the accepted value i.e. ± 25. Also the results passed accuracy, precision and trueness criteria which were assigned “accepted” status. However, it should be noted that all samples had positive biases. These positive biases caused by overestimate results which was surprisingly unexpected not to have some loss during chemical separation steps. Possibly it could be explained by inaccurate determined recovery yield. The recovery yield was determined from the metal titration method using Titriplex III (Na\(_2\)-EDTA, 2H\(_2\)O). The end point which solution colour was changed from red to orange-yellow, was not clearly observed. The relative biases were however within the MARB which obtained the “Accepted” status. The method could be improved in its accuracy by improving the recovery yield determination. Commonly mass spectroscopy such as AAS and ICP, could be a better choice to determine accurate yttrium recovery yield but the cost for analysis may be expensive.
Table 3. The performance evaluation of samples.

| Sample | S 2   | S 50  | S 100 | S 1000 |
|--------|-------|-------|-------|--------|
| Target value | 2.040 | 50.615| 100.495| 1008.537|
| Target unc  | 0.063 | 1.574 | 3.124 | 31.080 |
| MARB | 25 | 25 | 25 | 25 |
| Mea value | 2.252 | 59.210 | 117.254 | 1163.459 |
| Mea unc  | 0.230 | 3.220 | 5.720 | 49.044 |
| Rel bias | 10.36 | 16.98 | 16.68 | 15.36 |
| Accuracy | P | P | P | P |
| P | 10.69 | 6.27 | 5.78 | 5.22 |
| Precision | P | P | P | P |
| Value measured x 2.58$ho$ | 30.43 | 18.91 | 17.41 | 15.54 |
| Value target | P | P | P | P |
| Turness | P | P | P | P |
| Final score | P | P | P | P |

The performance of four concentration levels were proved to be successful using this analytical method which can be confirmed to determine activity concentration at low to high level in a range of 2 – 1000 Bq kg⁻¹ in 20 g dry marine animal samples. Moreover, it is important to note that the yttrium source samples were fairly purified as can be seen from yttrium activity decay with time in Figure 2.

![Figure 2. The Analysis of $^{90}$Sr determination](image)

The activity can be simply calculated according to equation (5) and (6).

$$A = A_0e^{-\lambda t}$$  \hspace{1cm} (5)

$$\lambda = \frac{ln2}{\tau}$$  \hspace{1cm} (6)

As can be seen from Figure 2, measured decay constant ($\lambda$) of the sample can be determined from the activity decay curve which was 0.263. This means the measured yttrium half-life was equal to 63.24 h which was closed to the theoretical one i.e. 64.2 h [11]. This can be validated that the radioanalytical method was effective to perform yttrium separation in marine animal samples.
4. Conclusion
The determination of $^{90}$Sr activity concentrations in a range from 2 to 1000 Bq kg$^{-1}$ in 20 g dry weight of mussel samples using the liquid extraction technique, 10% HDEHP and Cherenkov counting measurement was proved to be successful with a short period of time for source preparation in a few hours. All results passed accuracy, precision and trueness criteria and therefore obtained “Accepted” status with relative bias in range of 10.36 – 16.98, within accepted relative bias of ± 25%. This confirmed that $^{90}$Sr determination in marine animal samples especially with small mass of 20 g can be used to analyze low to high concentration range of 2-1000 Bq kg$^{-1}$ with both cases of radiation monitoring and radiological incident purposes. However the analysis results can be improved in accuracy by determining a highly accurate recovery yield from mass spectroscopy techniques such as AAS and ICP but the analysis cost would be increased.

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