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PROFICIENCY TEST RESULTS FOR STRONTIUM-90 ANALYSIS IN ENVIRONMENTAL MATRIX AT RADIOCHEMISTRY AND ENVIRONMENT LABORATORY, MALAYSIAN NUCLEAR AGENCY

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ABSTRACT

Strontium-90 (Sr-90) is a radioactive isotope with significant health risks due to its long half-life and bone-seeking properties. Accurate analysis of Sr-90 is essential for environmental monitoring and safety assessments. This study presents the proficiency test (PT) results conducted at the Radiochemistry and Environment Laboratory, Malaysia Nuclear Agency, in 2021 until 2023. A total of nine samples, including spiked water, simulated contaminated surfaces, and seawater, were analyzed by using a gas proportional counter for beta counting. The acceptability of results was rated based on the trueness and precision determined by the relative bias and P values. Four results fell within the acceptable range, one was in the warning range, and four were deemed unacceptable. The main causes of the unacceptable results were due to the lack of Y-90 correction, loss of Sr-90 during sample preparation, and possible incomplete separation of Sr-90. These findings emphasize the need for method refinement, enhanced quality control, and continuous laboratory training to improve the accuracy and reliability of Sr-90 analysis.

Keywords: strontium-90, proficiency test, radiochemistry

INTRODUCTION

Strontium-90 (Sr-90) is a radioactive isotope that is produced as a by-product of nuclear fission in reactors and nuclear weapon detonations. Due to its similarity to calcium, Sr-90 can replace calcium in bones, leading to serious health issues such as bone cancer and leukemia. Its long half-life of approximately 28.8 years means Sr-90 remains a persistent environmental contaminant, posing long-term risks to human health and the environment. The accurate detection and quantification of Sr-90 in various matrices is crucial for environmental monitoring, public health protection, and regulatory compliance.

The analysis of Sr-90 involves complex radiochemical procedures due to its low-energy beta emissions and the presence of other radionuclides in environmental samples. It can be measured using various techniques, i.e. beta counting, liquid scintillation spectrometry, and mass spectrometry (Vajda & Kim, 2010). Laboratories must employ precise and accurate methodologies to ensure reliable results. Proficiency testing (PT) is an essential quality assurance tool that evaluates the performance of laboratories in conducting specific analyses, providing an objective measure of their analytical capabilities. Participation in PT schemes enables laboratories to benchmark their performance against known values and other laboratories, identifying strengths and areas for improvement. The findings from these tests provide valuable insights into the analytical processes at the participating laboratory and highlight the importance of continuous quality control and method validation.

This study presents the results of PT conducted at Radiochemistry and Environment Laboratory (RAS) from the year 2021 to 2023 through two PT programmes, Analytical Laboratories for the Measurement of Environmental Radioactivity (ALMERA) and World-Wide. ALMERA PT program was provided by the IAEA Terrestrial Environmental Radiochemistry Laboratory (TERC) on determination of anthropogenic and natural radionuclides in water, soil and simulated contaminated surface samples. On the other hand, the World-Wide PT program was organized by the Radiometrics Laboratory (RML) of the IAEA Environment Laboratories to test the performance of participating laboratories in an analysis of radionuclides in a seawater sample.

The PT results highlight the critical role of accurate Sr-90 analysis in environmental monitoring and public health protection, as well as its significance at the national level for regulatory compliance, radiation safety, and policymaking. National agencies such as the Ministry of Health (MOH), the Department of Environment (DOE), and the Atomic Energy Department (JTA) rely on precise Sr-90 data for assessing contamination risks, ensuring food and water safety, and guiding radiation protection measures. This study serves as a benchmark for RAS's performance and guides future improvements.

MATERIALS AND METHODS

A total of nine samples were received from the International Atomic Energy Agency (IAEA) through two PT programmes, ALMERA and World-Wide. The details of the samples received are shown in Table 1. The spiked water was prepared using drinking water sourced from Seibersdorf, Austria and gravimetrically spiked with known amounts of a prepared standard solution, containing a mixture of certified radionuclides and acidified to < pH 2 (0.05M HNO_3) for stability.

The simulated contaminated surface with Sr-90 spiked magenta ink printed on the surface was prepared by the IAEA using in-house printing technique (International Atom Energy Agency, 2023). For seawater, 5 L of filtered Mediterranean Sea water was spiked by the IAEA with radionuclides H-3, Sr-90, Ba-133, Cs-134, Cs-137 and two undisclosed γ-ray emitters (International Atomic Energy Agency, 2024). All samples were sent to the laboratory via courier delivery.

Table 1. Details of the samples received

Year	PT Code	Sample No.	Sample Type
2021	IAEA-TEL-2021-04 Part II	2	Spiked water
2021	IAEA–RML–2021–01	S21N020	Seawater
2022	IAEA-TERC-2022-02 Part II	1, 2	Spiked water
2022	IAEA–RML–2022–01	S22N20	Seawater
2023	IAEA-TERC-2023-02	2	Spiked water
2023	IAEA-TERC-2023-02	5,7	Simulated contaminated surface
2023	IAEA–RML–2023–01	S23N020	Seawater

Sample Pre-treatment and Preparation

A volume of 10 mL of liquid PT sample (spiked water and seawater) was diluted with distilled water to 100 mL. For spiked water, 1.0 g of Sr^{2+} carrier (5 mg/g) was added to the 100 mL solution. For seawater, 0.175 mL of concentrated HNO_3 was added before the addition of Sr^{2+} carrier. The preparation of seawater was continued by adding 2 M NaOH until the pH of the solution increased to between pH 8 and 9. Next, about 1.0 g of Na_2CO_3 was added and the solution was left overnight to allow precipitation. The collected precipitate was dissolved in concentrated HNO_3 and then evaporated until dryness. After that, 100 mL distilled water was added into the solution to dissolve the residue and the sample was further acidified until pH 2 by using 3.0 M HNO_3. Simulated contaminated surface paper was cut and stuck to a 2.5-inch diameter planchet and was ready for counting.

Radiochemical Separation and Purification

Radiochemical separation and purification processes were carried out on the prepared spiked water and seawater samples. Radiochemical separation was done by using 2 mL of cation exchange resin, Dowex 50W-X8 (Na^+ form), 100-200 mesh. The resin was pre-conditioned by using 0.1 M HNO_3 before the sample was loaded into the resin. The beaker containing the sample was then rinsed with 5 mL of 0.1 M HNO_3 for three times followed by elution of Sr-90 using 8 M HNO_3. The solution collected was then evaporated to dryness and the residue was re-dissolved with 10 mL of 8 M HNO_3 and proceeded to the purification process.

Purification was done by using 0.7 g of Eichrom Sr resin (100 – 150 µm) that was pre-conditioned by using 5 mL of 8 M HNO_3. After the sample was loaded into the column, 5 mL of 3 M HNO_3–0.05 M oxalic acid solution was added. Then, the column was rinsed with 5 mL of 8 M HNO_3. Sr-90 was then eluted by using 10 mL of 0.05 M HNO_3. The Sr purified solution was transferred to the counting planchet and dried.

Sample Counting

The sample was counted for 100 minutes, in 3 cycles by using a gas proportional counter of Automatic Low Background Alpha/Beta Counting System (S5XLBPF, Canberra Inc., USA) as shown in Figure 1. The alpha and beta plateau of the system were set using Am-241 and Sr-90 plated disc standard sources, respectively, to establish the measurement conditions. The counting efficiency of Sr-90 was determined by using a series of Sr-90 standards prepared at different activities (0.5 Bq – 4 Bq).

Figure 1. Low background gross alpha beta counting system

Data Analysis

The data were analysed based on the report by Wan Mahmood & Abdullah (2020). The chemical yield for Sr based on residual weight resulting from the addition of a stable Sr carrier, Sr^{2+} ($Sr(NO_3)_2$) was calculated using equation below:

$$y_{Sr}(\%) = \frac{[(Rd)\ (x/z)]\ (1000)\ (100)}{(Cc)(wc)} \qquad (1)$$

where,

Y_{Sr}:	chemical yield for strontium (%)
Rd:	dried weight residue in the planchet (g)
x:	molecule weight of strontium (87.62 g/mol)
z:	molecule weight of $Sr(NO_3)_2$ (211.63 g/mol)
Cc:	concentration of strontium carrier, Sr^{2+} (mg/g)
wc:	weight of added strontium carrier, Sr^{2+} (g)

The Sr-90 activity concentration calculated in the liquid sample is expressed in Bq/L. All nuclear data used in the calculation of Sr-90 activity concentration are taken from the data suggested in the Chart of the Nuclides (Magill et al, 2006). Sr-90 activity concentration is calculated using the count per minute (CPM) values for the sample and the background obtained from the beta counting data generated. The Sr-90 activity concentration reported in the results is a specific activity concentration during the reference date and it is calculated based on the equation below:

e-JSNM

$$A = \frac{(CPMgs - CPMbg)(e^{\lambda t})(1000)}{(60)(Esr)(Ysr)(Wdw)} \qquad (2)$$

where,

A: Measured activity concentration of Sr-90 at sampling date (Bq/kg dry wt. or Bq/L)
CPMgs: CPM value for Sr-90in the sample (CPM)
CPMbg: CPM value for background (CPM)
λsr: decay coefficient = ln 2/t1/2 (28.5 years)
t: elapsed time from the reference date and time to the counting date and time (year)
Esr: Sr-90 counting efficiency
Ysr: chemical yield of strontium
Wdw: sample dry weight

The calculation of the combined uncertainty value for the Sr-90 activity concentration measurement in the sample on the reference date is based on equation (2) as discussed above. Thus,

$$U(A) = (A)\left[\sqrt{[(U(n^{s}_{90Sr})/n^{s}_{90Sr})^2 + (U(t)/t)^2 + (U(\lambda_{Sr})/\lambda_{Sr})^2 + (U(E_{Sr})/E_{Sr})^2 + (U(Y_{Sr})/Y_{Sr})^2 + (U(W_{dw})/W_{dw})^2]}\right] \qquad (3)$$

Where,

U(A): uncertainty value for Sr-90 activity concentration measured at reference date (Bq/L)
A: Sr-90 activity concentration measured at reference date (Bq/L)
$U(n^{s}_{90Sr})$: uncertainty value of net CPM of Sr-90 (CPM)
n^{s}_{90Sr}: net CPM of Sr-90 (CPM)
U(t): uncertainty value for elapse time from the date and time of sampling to date and time of counting (year)
t: elapse time from the reference date and time to date and time of counting (year)
$U(\lambda_{Sr})$: uncertainty value for decay coefficient of Sr-90 (year-1)
λ_{Sr}: decay coefficient of Sr-90 (year-1)
$U(E_{Sr})$: uncertainty value for Sr-90 counting efficiency
E_{Sr}: Sr-90 counting efficiency
$U(Y_{Sr})$: uncertainty value for a chemical yield of Sr-90
Y_{Sr}: chemical yield of Sr-90
$U(W_{dw})$: uncertainty value of sample dry weight
W_{dw}: sample dry weight

Result Evaluation

The evaluation follows the methodology applied for the annual IAEA proficiency testing schemes in the areas of radionuclide measurements and trace element analysis. The trueness of the result was based on the relative bias calculated from equation:

$$Bias_{relative} = \frac{Value_{reported} - Value_{target}}{Value_{target}} \ x \ 100\% \quad (4)$$

The relative bias is the relative difference between the reported and the target value and is compared to the Maximum Acceptable Relative Bias (MARB) which has been determined for each property value, considering the analytical methods, the analyte level in the sample and the complexity of the analysis. The result will be rated "Accepted (A)" for trueness when the value of relative bias is lesser than MARB.

The precision was evaluated based on the P value that corresponds to the relative combined uncertainty of the relative bias, calculated in Equation (4).

$$P = \sqrt{\left(\frac{U_{target}}{A_{target}}\right)^2 + \left(\frac{U_{reported}}{A_{reported}}\right)^2} \times 100\% \qquad (5)$$

Where,
U_{target}: uncertainty of target value
A_{target}: activity of target value
$U_{reported}$: uncertainty of reported value
$A_{reported}$: activity of reported value

The relative bias is then compared to the expanded uncertainty of the relative bias:

$$|Bias_{relative}| \leq k \times P \qquad (6)$$

Where,
k: the coverage factor, 2.58 for a level of confidence of 99%
P: P value from Equation (5)

When the above criterion is fulfilled, the reported result is not significantly different from the target values considering the uncertainties associated with both values. The reported uncertainty of measurement is large enough to cover the bias of the method. Aside from that, the P value is also compared to the MARB and must be less than the MARB. When both criteria related to the measurement uncertainty are fulfilled, the reported result for precision is rated "accepted (A)”. The result is rated "Not Accepted (N)" for precision if either of the two conditions are not fulfilled.

The final score is assigned according to the detailed evaluation described above. The possible scores are "Accepted (A)" when both, trueness and precision were rated "Accepted", "Not Accepted (N)" when the trueness rating is "Not Accepted" and "Warning (W)" when the trueness rating is “Accepted” but the precision rating is "Not Accepted".

RESULTS AND DISCUSSION

The PT results for Sr-90 analysis in seawater samples from 2021 to 2023 are summarized in Table 1. The table includes the assigned values, reported values, relative bias, P values, and final scores for three seawater samples received in 2021 (S21N020), 2022 (S22N020), and 2023 (S23N020).

Table 1. Sr-90 analysis results for seawater samples

Sample No.	Assigned Value (Bq/L)	Reported Value (Bq/L)	Relative Bias (%)	P value (%)	Final Score
S21N020	0.618 ± 0.005	0.744 ± 0.045	20.4	6.0	Warning
S22N020	0.816 ± 0.007	0.770 ± 0.050	-5.6	6.5	Accepted
S23N020	0.708 ± 0.006	0.446 ± 0.027	-36.9	6.1	Not Accepted

The PT results for the seawater samples show varying levels of performance in Sr-90 analysis. The seawater samples were prepared using the precipitation method, which may have influenced the recovery of stable Sr carrier and contributed to the observed biases in reported activities. The reported value for sample S21N020 of 0.744 Bq/kg was 20.4% higher than the assigned value of 0.618 Bq/kg, resulting in a final score of "Warning." The P value of 6.0% indicates a marginally acceptable performance, suggesting that the laboratory's methodology may need adjustments to improve accuracy. The significant positive bias suggests potential issues in sample preparation or measurement processes, and the precipitation method used for sample preparation might have contributed to reduced recovery, leading to an overestimation of activity.

In contrast, the reported value of 0.770 Bq/kg in sample S22N020 was within 5.6% of the assigned value of 0.816 Bq/kg, and this result was accepted with a P value of 6.5%. This sample demonstrated the laboratory's ability to produce accurate and reliable results for Sr-90 in seawater. The minor negative bias indicates that while the results are close to the assigned value, there may still be slight underestimation that needs to be addressed.

The reported value of 0.446 Bq/kg in sample S23N020 showed a significant negative bias of -36.9% compared to the assigned value of 0.708 Bq/kg, resulting in a final score of "Not Accepted." The P value of 6.1% indicates an unsatisfactory performance, highlighting substantial inaccuracies in the laboratory's analysis for this sample. This significant underestimation suggests issues such as incomplete radiochemical separation or overestimation of the analysis efficiency. Additionally, the precipitation method used in sample preparation may have led to reduced recovery, further contributing to the underestimation of activity.

The PT results for Sr-90 analysis in spiked water samples from 2021 to 2023 at RAS are summarized in Table 2.

Table 2. Sr-90 analysis results for spiked water samples

Sample No.	Assigned Value (Bq/L)	Reported Value (Bq/L)	Relative Bias (%)	P value (%)	Final Score
2/2021	146.8 ± 8.4	248.5 ± 14.9	69.28	8.29	Not Accepted
1/2022	26.4 ± 0.007	23.66 ± 2.91	-10.38	13.71	Accepted
2/2022	7.42 ± 0.45	6.64 ± 0.82	-10.51	13.76	Accepted
2/2023	14.2 ± 0.7	13.92 ± 0.88	-2.0	8.02	Accepted

The reported value of 248.5 Bq/kg in Sample 2/2021was 69.28% higher than the assigned value of 146.8 Bq/kg, resulting in a final score of "Not Accepted" with a P value of 8.29%. This significant positive bias indicates substantial overestimation, suggesting possible issues in sample preparation, contamination, or measurement errors. This result highlights a critical need for method refinement and strict quality control to prevent such discrepancies in future analyses.

For the PT result in 2022, the reported value of 23.66 Bq/kg in sample 1/2022 showed a relative bias of -10.38% compared to the assigned value of 26.4 Bq/kg, with a final score of "Accepted" and a P value of 13.71%. Although the result is within acceptable limits, the negative bias indicates a slight underestimation, pointing to potential areas for improvement in the laboratory's analytical processes to enhance accuracy further. Similar to Sample 1/2022, the reported value of 6.64 Bq/kg for Sample 2/2022 showed a negative bias of -10.51% relative to the assigned value of 7.42 Bq/kg. With a P value of 13.76% and an "Accepted" score, this result indicates acceptable performance but suggests the need for minor adjustments to reduce bias and improve the accuracy of low-level Sr-90 measurements.

In 2023, the result for spiked water showed a significant improvement. The reported value of 13.92 Bq/kg closely matched the assigned value of 14.2 Bq/kg, with a relative bias of -2.0% and a P value of 8.02%. This result was "Accepted," demonstrating the laboratory's improved accuracy and precision in Sr-90 analysis. The minor negative bias suggests a successful enhancement of analytical methods and quality control procedures over the testing period.

The proficiency test results for Sr-90 analysis in simulated contaminated surface samples from 2023 are summarized in Table 3.

Table 3. Sr-90 analysis results for simulated contaminated surface samples

Sample No.	Assigned Value (Bq/sample)	Reported Value (Bq/sample)	Relative Bias (%)	P value (%)	Final Score
5/2023	2.25 ± 0.10	8.37 ± 0.11	272.0	4.63	Not Accepted
7/2023	4.52 ± 0.22	10.19 ± 0.12	125.4	5.01	Not Accepted

The proficiency test results for the simulated contaminated surface samples indicate significant discrepancies in the reported Sr-90 values compared to the assigned values, resulting in "Not Accepted" scores for both samples. The reported value of 8.37 Bq/sample in Sample 5/2023 was 272.0% higher than the assigned value of 2.25 Bq/sample, resulting in a P value of 4.63% and a final score of "Not Accepted." For Sample 7/2023, the reported value of 10.19 Bq/sample was 125.4% higher than the assigned value of 4.52 Bq/sample, with a P value of 5.01% and a final score of "Not Accepted". This substantial positive bias indicates a severe overestimation in the Sr-90 analysis.

A key factor contributing to this overestimation is the presence of Yttrium-90 (Y-90), the decay product of Sr-90. Y-90 has a half-life of approximately 64 hours and reaches secular equilibrium with Sr-90 in about three weeks. At equilibrium, the total beta activity measured will be nearly double the activity of Sr-90 alone because both Sr-90 and Y-90 contribute equally to the beta emissions. If Y-90 is not properly accounted for, the reported Sr-90 activity can be significantly overestimated.

Unlike liquid samples, which require radiochemical separation to isolate Sr-90, surface samples are analyzed by direct counting using a gas proportional counter. Since no chemical separation is performed, the analysis entirely depends on the instrument's efficiency and the ability to consider all factors affecting the determination of Sr-90 radioactivity from the beta counts. Proper consideration of Y-90 equilibrium with Sr-90 is crucial to prevent overestimation. Since Y-90 contributes to beta activity, its presence must be accounted for when interpreting results. Other important factors that strongly affect the determination of Sr-90 in surface samples is the difference in calibration source and sample geometry. Calibration was carried out by using distributed plated surface while surface samples is printed paper which have a different surface composition, thickness, and uniformity. Differences in material properties can affect beta energy attenuation and scattering causing over- or underestimation of beta counts. Aside from that, ensuring accurate background subtraction is essential, as fluctuations in background radiation can influence the measured beta activity.

The mixed results from the sample analyses indicate the need for continuous improvement in the laboratory's procedures. The accepted result demonstrates that the laboratory at RAS has the potential to perform accurate Sr-90 analyses. However, the warning and not accepted scores highlight inconsistencies that must be addressed.

CONCLUSION

The proficiency test results for Sr-90 analysis at RAS revealed that only 4 out of 9 samples met the acceptance criteria. While this demonstrates the laboratory's capability to achieve accurate Sr-90 measurements under certain conditions, the results also highlight critical areas that require improvement. The instances of warnings and failures indicate inconsistencies in analytical procedures, potential issues in radiochemical separation, and limitations in measurement processes that must be addressed to enhance overall reliability and accuracy. To improve performance, RAS should refine its analytical techniques to minimize errors, particularly in radiochemical separation methods for liquid samples and correction for Y-90 interference in direct counting of surface samples. Additionally, enhancing calibration procedures to accurately reflect real sample conditions will help reduce systematic biases. Continuous participation in PT schemes and adherence to international standards will be crucial in maintaining and improving the laboratory's analytical performance.

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