Developed Method for Better Detection of Radionuclides in Plants by Gamma Spectrometry

Ahmed El-Sharkawy, Hanan Al-Ghamdi, Hekmat El-Begawy

Abstract— As a result of a previous fail in the International Atomic Energy Agency intercomparison (IAEA-TEL-2012-03) for the determination of the activity concentration of 137Cs in hay sample, the major source of error in determining the photopeak efficiency of the 661.6 keV gamma energy line of the 137Cs was due to the difficulties to reproduce the same matrix and elemental composition of the certified reference calibration materials as that of the hay sample. New approach was developed through the digestion of the ashed plant sample and delivers a clear small volume sample solution into the standard counting container for gamma measurements. The activity of the target radionuclide was determined by comparison with an acidified deionized solution spiked with known amounts of the typical radionuclide and 133Ba as a yield tracer in identical conditions. Method validation was established by analyzing replicates of the IAEA-TEL-2012 hay sample and the IAEA-372 grass sample for 137Cs. The validation was established using several parameters; accuracy, precision and bias in order to ensure that it fits for the purpose. Trueness was evaluated in terms of relative bias, and no significant deviations from the true values due to samples densities and/or matrix-variation effect were found. The closeness of the determined 137Cs activities to the target values was evaluated in terms of accuracy, and was found to have an average of 0.98. The precision of the method is found to be fairly good, with uncertainties less than 7%. It can be concluded that the method is capable of providing high accuracy and precision measurements of 137Cs in plant samples. Also, it may be recommended that better detection limits for 226Ra and 228Ra activities in environmental plant samples can be achieved with this method using bulk plant samples.

Index Terms— Plants, ^{137}Cs, IAEA proficiency test, plants digestion, Gamma spectrometry.

I. INTRODUCTION

Gamma-ray spectrometry is one of the most widely used techniques to determine the activity concentrations of ^{226}Ra, ^{228}Ra, ^{40}K and ^{137}Cs in plants and vegetation samples. High purity germanium detectors (HPGe) are commonly used to obtain a precise quantitative assessment of the specific activities of these radionuclides. In principle, efficiency calibration of the germanium detector is often carried out with reference sources of equivalent geometry (marinelli beakers or plastic containers filled into laboratory-defined volumes) and density [1]. The presence of considerable variations in plant and vegetation samples densities and elemental composition, and the lack of the availability of different calibration reference sources for each type of plant samples, has initiated the need of applying corrections for the

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self-absorption [2], [3]. Several experimental methods have been reported for the correction of self-absorption in bulk samples [4]-[6]. Other mathematical methods, including Monte Carlo simulations were also reported [7]-[10]. For better assay of the specific activities of gamma emitting radionuclides in plants and vegetation samples, many factors have to be considered; sufficient quantities must be collected, limited packing volume of the dry ash, enough counting time, geometry and self-absorption due to differences in density and matrix. The laboratory result of the specific activity of ^{137}Cs in the IAEA-TEL-2012-03 hay sample was not accepted due to the use of IAEA certified reference plant samples to determine the 661.6 keV peak efficiency, and those reference materials differ in density and matrix from the unknown sample. The approach described in this work is to extract the target radionuclide from the ashed samples by acid dissolution and transfer the sample solution to the gamma counting container. The limited volume of the sample solution eliminates self-absorption due to density and elemental composition of the sample matrix, and improves the efficiency of the measurements.

II. METHODOLOGY

2.1 Materials and Apparatus

Gamma measurements were carried out using Canberra HPGe coaxial detector (Model GC4020) with 40% relative photopeak efficiency and 2.0 keV energy resolution at the 1332.5 keV gamma energy line of ^{60}Co. The detector was connected to a Canberra Digital Spectrum Analysis model DSA-1000. Plastic PV containers with a diameter of 7 cm and 5.5 cm height were utilized in the gamma measurements. Cesium-137 and Barium-133 were supplied by National Physics laboratory, UK (NPL-R03-01) and North American Technical Services, USA (NATS-EZ-83879-767) respectively. The gamma measurements and radiochemistry were carried out in 2013 at the laboratories of Technology Experts Co., Riyadh, Kingdom of Saudi Arabia (KSA).

2.2 Samples Treatment & Measurements

The plant samples are dried in an oven at 100° C for at least 24 hours. The dried samples are kept in a furnace at 400°C, it is then grinded and mixed thoroughly, transferred to a glass beaker and 1M HNO_3 is added to produce slurry. The samples are stirred for 1 hour, Ba-133 tracer is added and samples are stirred overnight. The radionuclides are leached out from the matrices by a mixture of concentrated nitric and hydrochloric acids under heating and stirring for 4 hours. This step is may be repeated and the supernatants are combined. If considerable solids remain, the solutions are transferred to another beaker and additional reflux on a hot plate (180-200°C) without stirring for 6-12 hours is carried out with occasional addition of H_2O_2 drops [11]-[13]. The combined

supernatants and the filtrate (if filtration was needed) solution volume is minimized by gentle evaporation and transferred to a defined volume of the gamma counting container. The activity of the target radionuclide is calculated by comparison with acidified deionized water standard sample spiked with a known amount of ^{133}Ba and ^{137}Cs, the target radionuclide, in identical conditions (container, volume, counting time, and detector). In this study we used ^{137}Cs as an example for determining the activity concentration and the related uncertainty, as ^{137}Cs is one of the most frequently measured radionuclide in environmental samples.

2.3 Quality Assurance

The micropipettes were carefully calibrated using a 5-digits calibrated sensitive balance. All reagents used were of analytical grade. Replicate measurements of the ^{137}Cs standard in the defined volume of the counting container were carried out. Replicate samples of the IAEA-TEL-2012-03-sample 04 and IAEA-372 grass sample were analyzed following the same procedure. Accuracy, bias and precision were determined for the associated replicate measurements. For the estimation of uncertainty, errors were propagated due to photopeak counts, standard tracers activities, sample weight and volume.

III. RESULTS & DISCUSSION

The activity concentration of ^{137}Cs in Bq/kg dry weight was determined in three replicates of the IAEA-TEL-2013-03 hay sample as presented in fig. 1. The determined activities of ^{137}Cs were decay corrected back to the reference date of the analyzed sample.
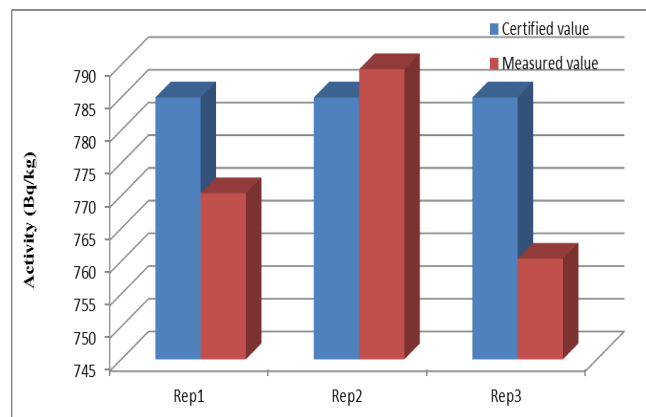
Fig. 1: Activties of ^{137}Cs in the IAEA-TEL-2012 hay sample (Bq/kg dry weight)

The mean value of the ^{137}Cs activity concentration was 773.3 Bq/kg dry weight. The limited variations between the three measurements may be explained by the differences in determining the peak area of the 661.6 and 356 keV gamma energy lines of the ^{137}Cs and ^{133}Ba respectively. The determined activity concentration of ^{137}Cs in this hay sample through the IAEA proficiency test was 985.0 ± 40 Bq/kg. The 661.6 keV photopeak efficiency was determined using three different fine grinded IAEA reference materials which were packed in identical volume of the measuring container. Comparing with previous work with the new digestion method results, it can be noticed that the elimination of errors arising from densities and matrices by the plant digestion approach improves the accuracy of results. For the validation of this new plant digestion procedure, four replicates of the IAEA-372 grass sample equal portions were analyzed for ^{137}Cs following the same new digestion method, and the results are presented in fig. 2.
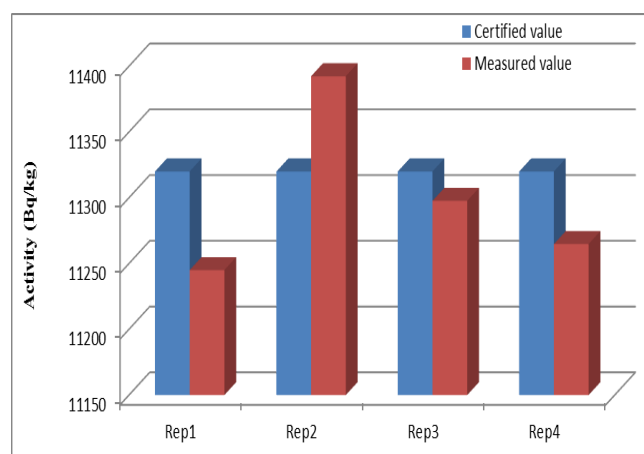
Fig. 2: Activties of ^{137}Cs in the IAEA-372 grass sample (Bq/kg dry weight)

As can be noticed from fig. 2, there are no large discrepancies between the four measurements, and the determined activities of ^{137}Cs are in good agreement with the target value within the associated uncertainties. Table 1 presents the previous IAEA-TEL-2012 intercomparison result of the ^{137}Cs activity in hay sample (IAEA-TEL-2012-I), the mean value of the ^{137}Cs activity in the same sample after applying the new digestion method (IAEA-TEL-2012-II) and the ^{137}Cs mean activity in the IAEA-372 grass sample.

Table 1: Accuracy and precision of the replicate measurements of the IAEA hay and grass samples

Sample	IAEA Value Bq/kg	IAEA Unc.	Lab Value Bq/kg	Lab Unc.	Lab Unc. %	Rel. Bias %	Accuracy	Precision %
IAEA-TEL-2012-I	785	24	985	40	4.0	25.4	1.2	5.0
IAEA-TEL-2012-II	785	24	773.3	50.6	6.5	-1.5	0.98	7.2
IAEA-372	11320	360	11281	645.7	5.7	-0.2	0.99	6.5

As for a new method being developed, accuracy, bias and precision have been evaluated [14], [15]. It is noticed from table 1 that the accuracy values are 0.98 and 0.99, which are highly accepted taking into consideration the associated uncertainties. The bias was calculated as a relative bias between the reported result and the target value [16]:

$$Rel. Bias \% = \frac{(Reported\ Value - Target\ Value)}{Target\ Value} \times 100$$

The relative bias values are -1.5 and -0.2, which indicates that there is no significant bias in this method. The method precision among the samples replicates expressed in the relative standard deviation has the values of 7.2% and 6.5% which is considered to be fairly good.

IV. CONCLUSION & RECOMMENDATIONS

Laboratory developed method was carried out to determine the activity concentration of ^{137}Cs in plant samples by gamma spectrometry using high purity germanium detector. The reason for this study was to eliminate the measurements errors from the self-absorption due to the variations in densities and matrices between the reference plant samples utilized in the efficiency calibration and the unknown samples. Replicates of IAEA hay and grass samples were analyzed for ^{137}Cs by drying, ashing, treatment the dry ash with mineral acids and transfer the cesium solution into the gamma counting container. The activity concentration of ^{137}Cs in the IAEA hay and grass samples was determined by comparison with a solution spiked with ^{137}Cs and ^{133}Ba as a yield tracer. The reliability and accuracy of this method was validated by the estimation of the precision which had the values of 7.2% and 6.5% for the hay and grass samples respectively. The accuracy of the method had an average value of 0.98. The relative bias percentages are -1.5 and -0.2, which present non-significant bias in this method. It can be concluded that the method is capable of providing high accuracy and precision measurements of ^{137}Cs in plant samples. Better detection limits for ^{226}Ra and ^{228}Ra activities in environmental plant samples can be achieved with this method using bulk plant samples.

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